



ÉCOLE POLYTECHNIQUE  
FÉDÉRALE DE LAUSANNE

*Electronic and Molecular Structure  
of Excited Ruthenium Polypiridyl Complexes  
From Picosecond X-Ray Absorption Spectroscopy*

Christian Bressler

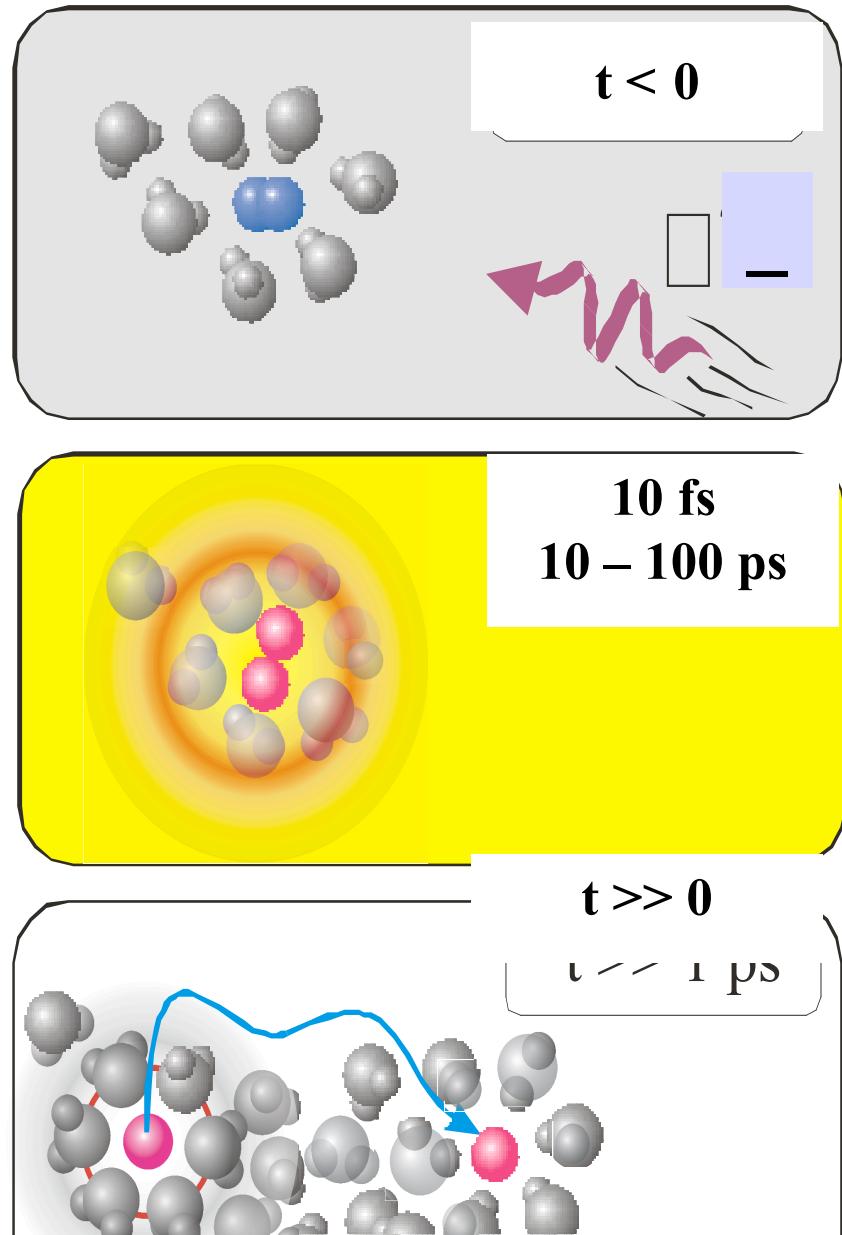
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Institut de Chimie Moléculaire et Biologique

Faculté des Sciences de Base

# What is *Structural Dynamics* about ?



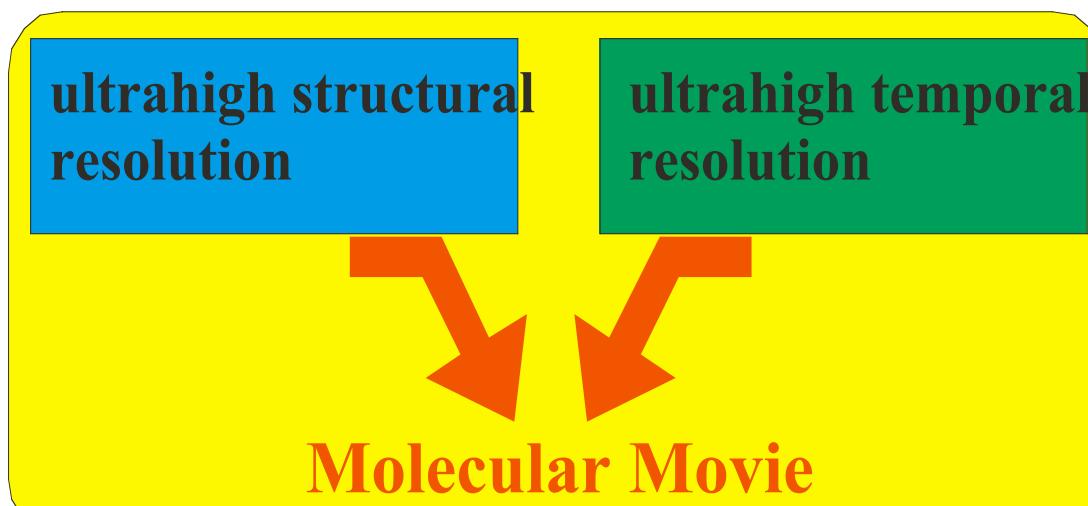
- **Electronic structure changes** are the primary event in all chemical, biological and physical processes
- These changes trigger or accompany (in non-adiabatic processes) **geometric structural changes**, i.e. nuclear motion

# *Electron transfer reactions*

- Fundamental in Chemistry and Biology
- Rates depend critically on the coupling of the electron motion to the nuclear motions within the molecule and/or with the solvents
- Short-lived reaction intermediates

GOAL:

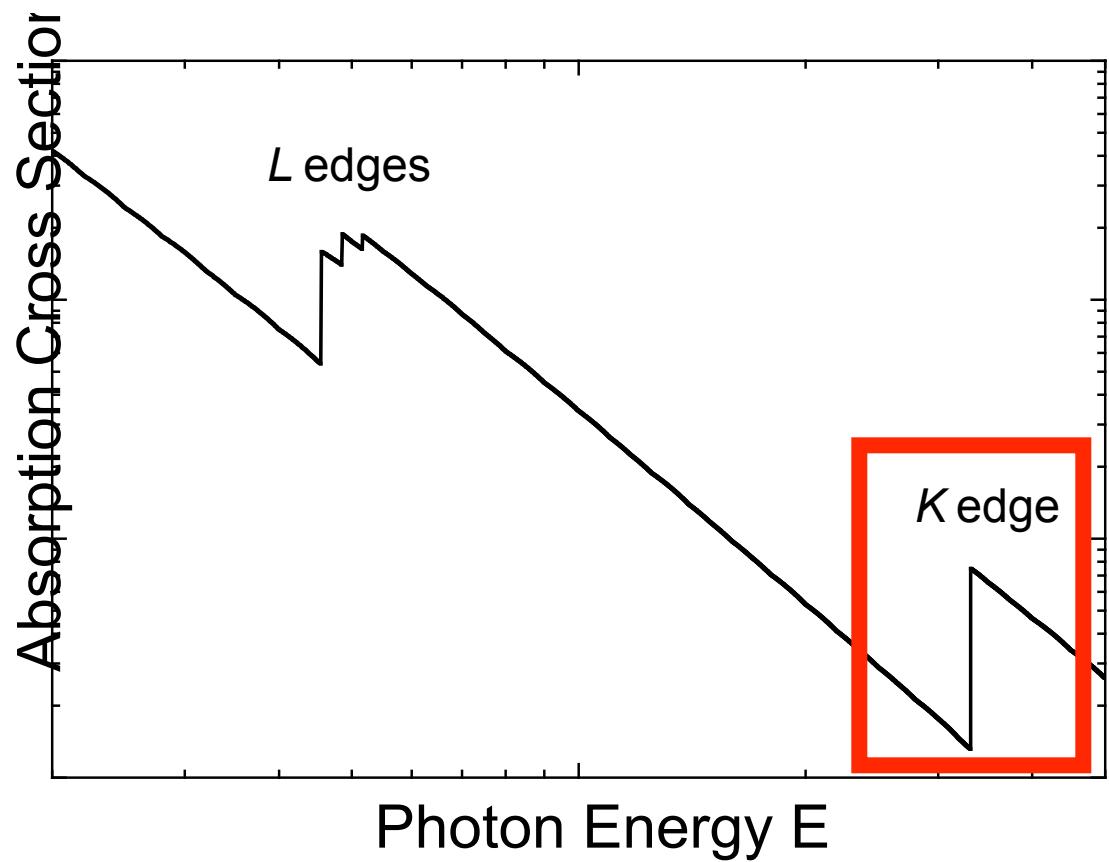
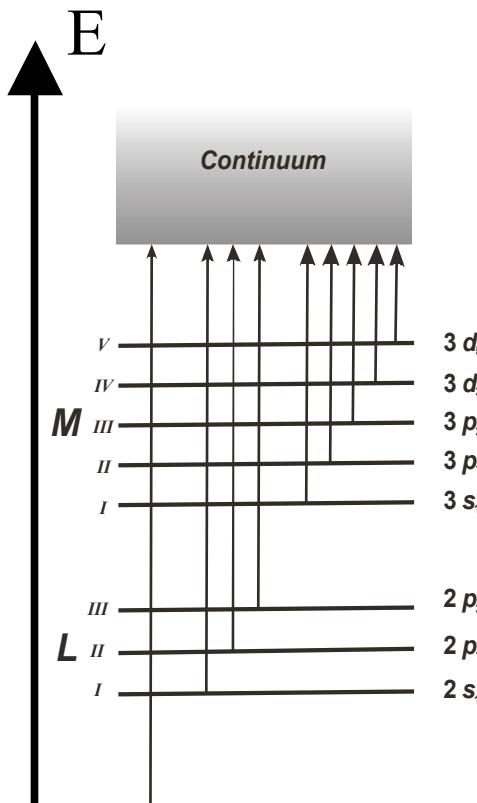
→ Create a molecular movie of the chemical reaction including the transition state(s) (need structural tools)



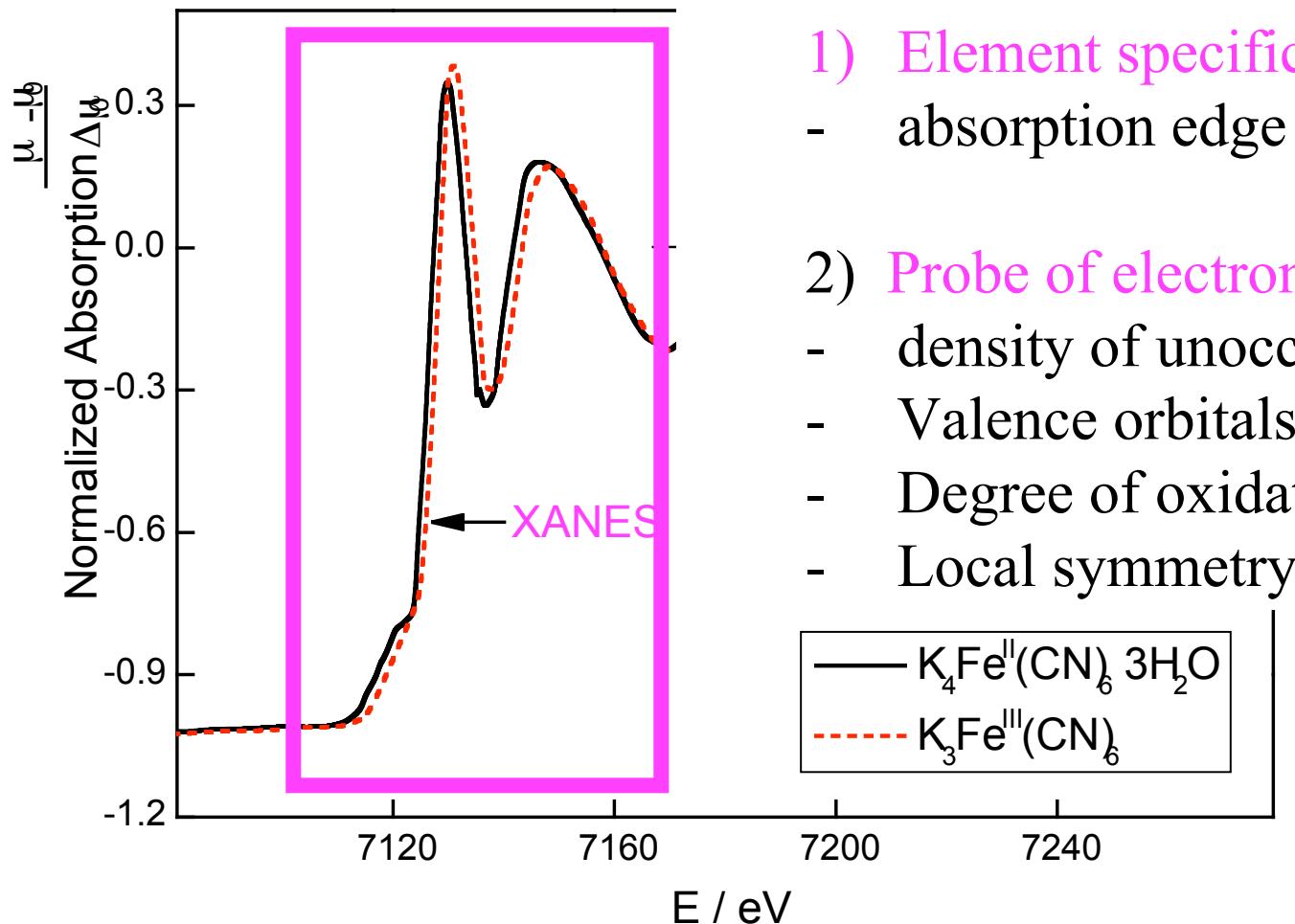
# Structural Tools

- Electron Diffraction (Gas Phase and Surfaces)
- Neutron Scattering (Low Z Elements)
- X-Ray Diffraction (Long-range order)
- **X-Ray Absorption** (Local geometric and electronic Structure)

# *X-Ray Absorption: Overview*



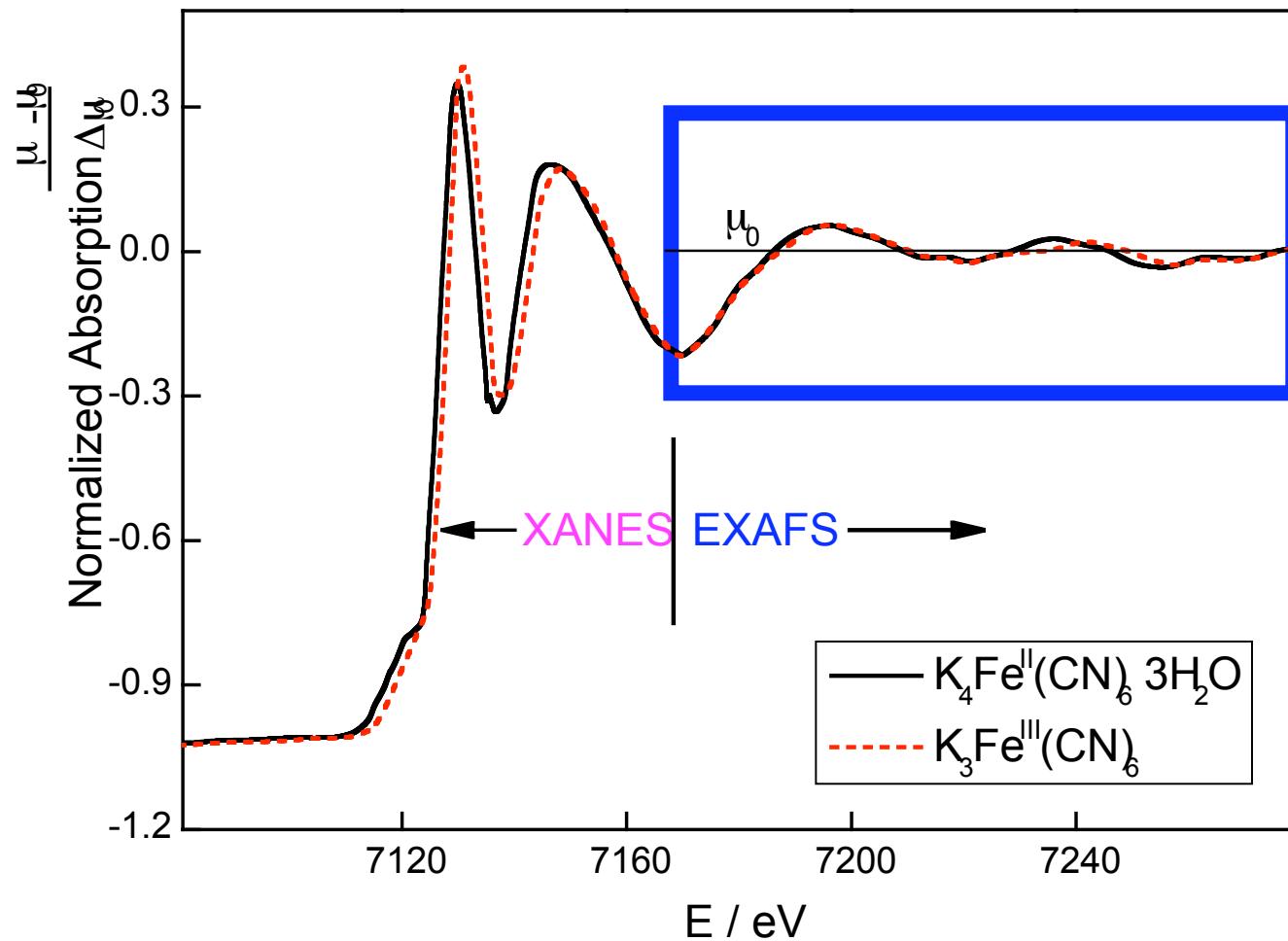
# *X-Ray Absorption: Overview*



- 1) Element specific:
  - absorption edge
- 2) Probe of electronic structure:
  - density of unoccupied states
  - Valence orbitals
  - Degree of oxidation
  - Local symmetry

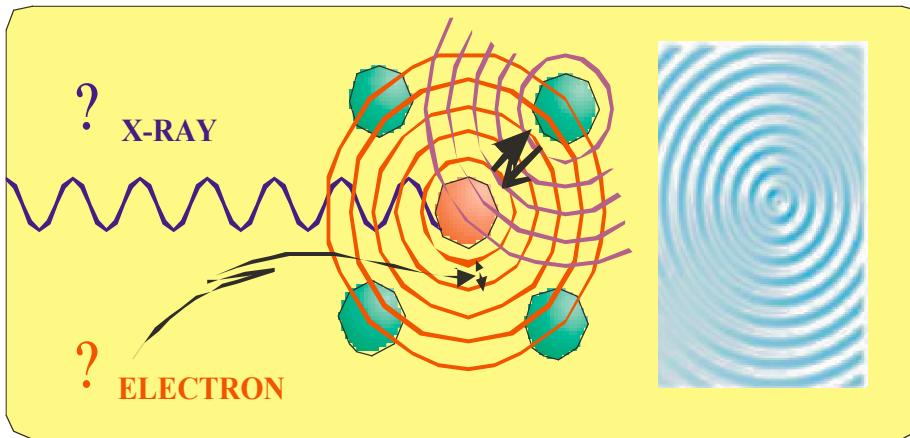
**X-ray absorption Near Edge Structure**

# *X-Ray Absorption: Overview*



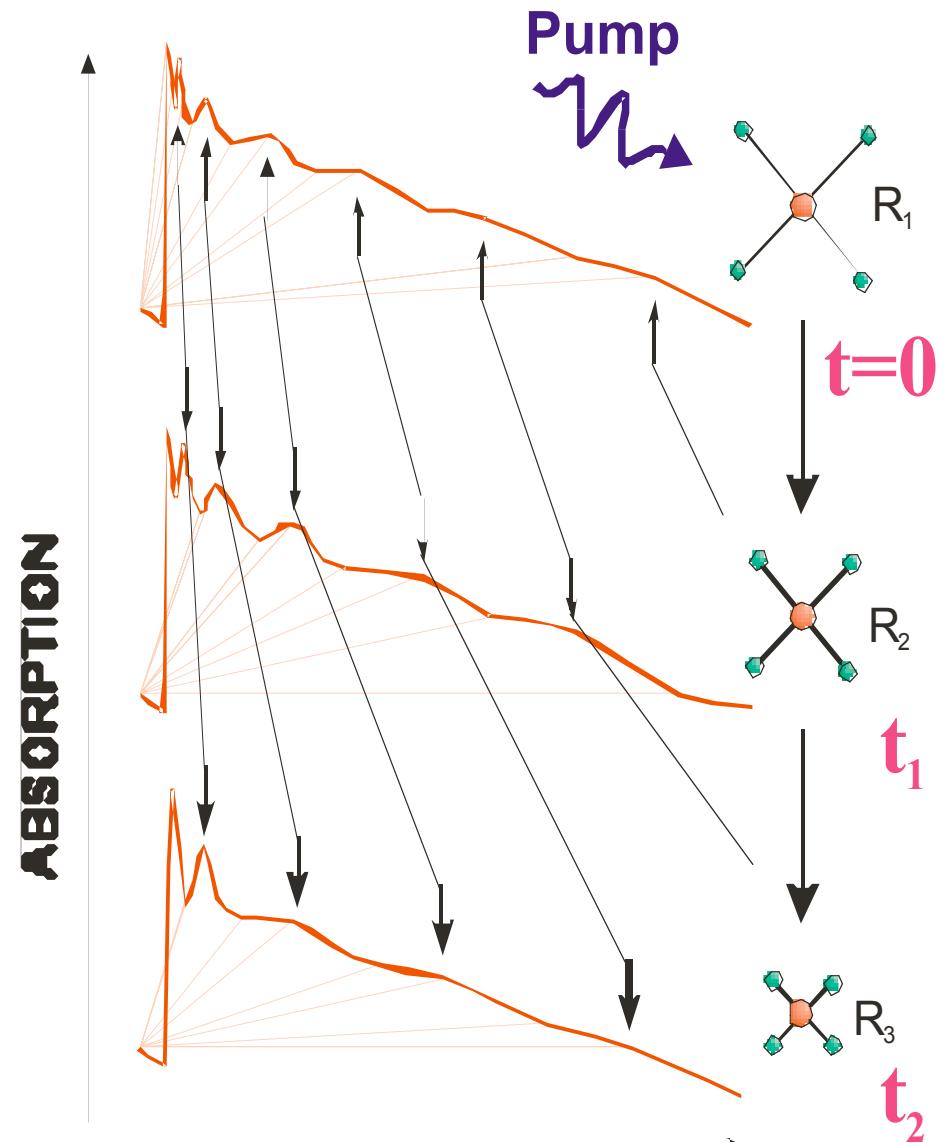
**Extended X-ray Absorption fine structure**

# *Time-Dependent* Structures via XAFS



- *Local Probe*
- Element - Specific

→ Study Time-Dependent  
Structures in Disordered  
Media



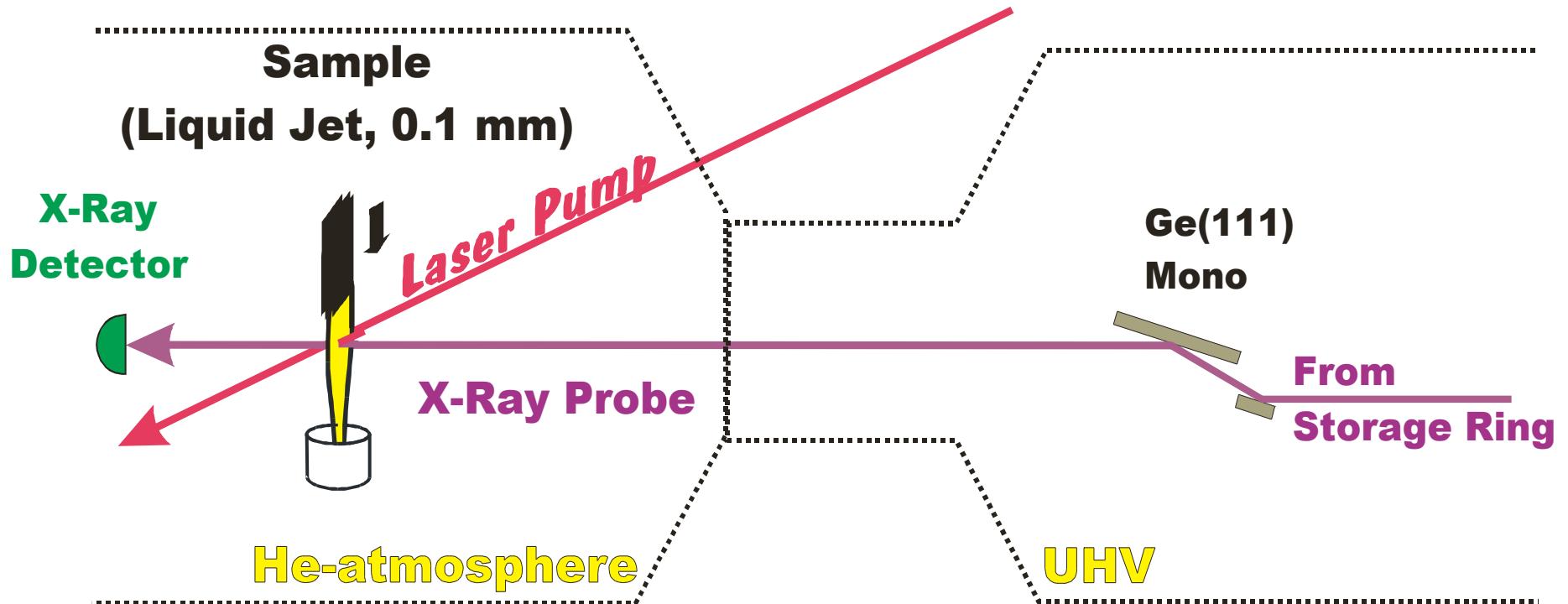
Distance and Angles (= *Structure*) in one single XAS scan

# Ultrafast X-Ray Absorption Spectroscopy

**short time scales  $\leftrightarrow$  short distance scales**

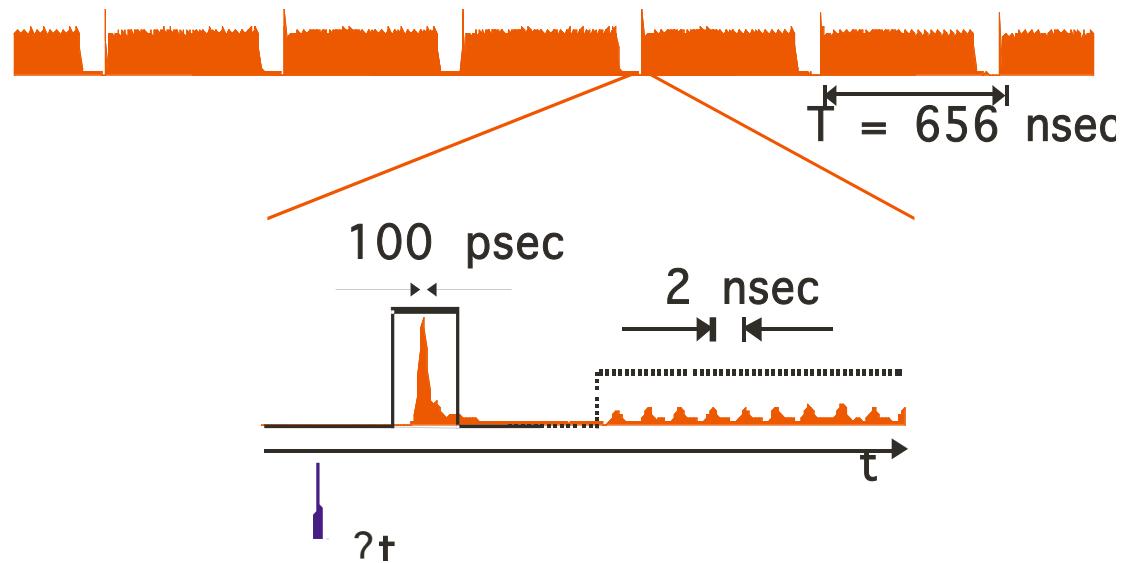
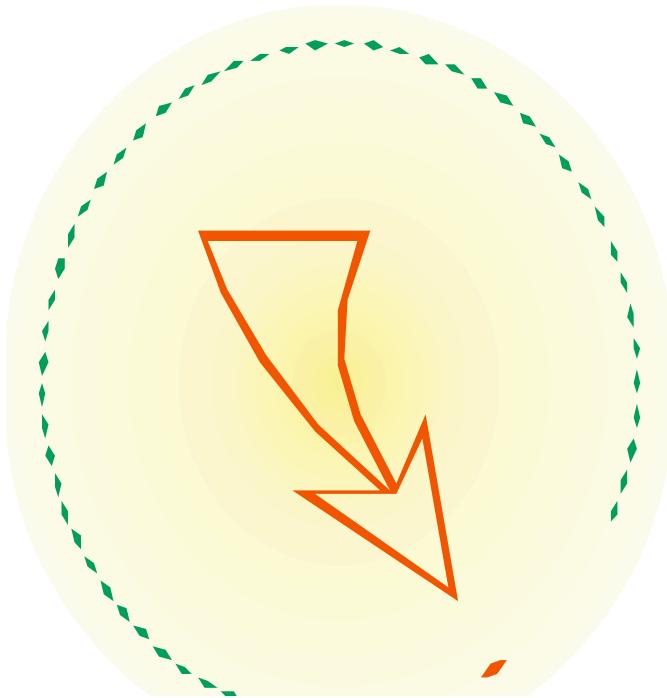
- 1) Detect both **electronic** and **structural changes** in condensed phases
- 2) No **long-range order**: dilute disordered media, surfaces, and the gas phases
- 4) **Chemical Selectivity**: mixed systems

## EXPERIMENTAL SETUP AT BEAMLINE 5.3.1 (ADVANCED LIGHT SOURCE)



- work in *disordered/dilute* systems
- sample refreshed every shot → **non-reversible** systems

# Data Acquisition Strategy



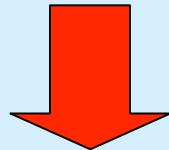
- synchronize two independent sources
- maintain control of chosen time delay

# Measuring at the Shot-Noise Limit

Beamline Specification (Source):

$$1 \times 10^{12} \text{ photons / s / } 0.1\% \text{ BW}$$

Beamline Transmission  
(M1, mono, filters, sample)

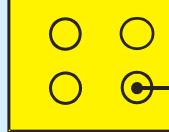


Single Pulse Intensity:

$$\approx 350 \text{ photons / pulse / } 0.03\% \text{ BW}$$

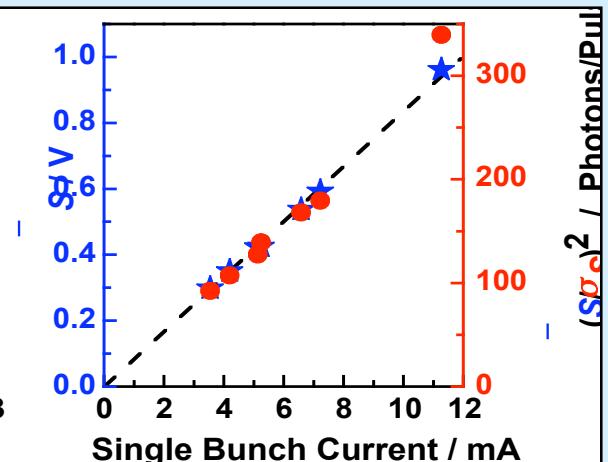
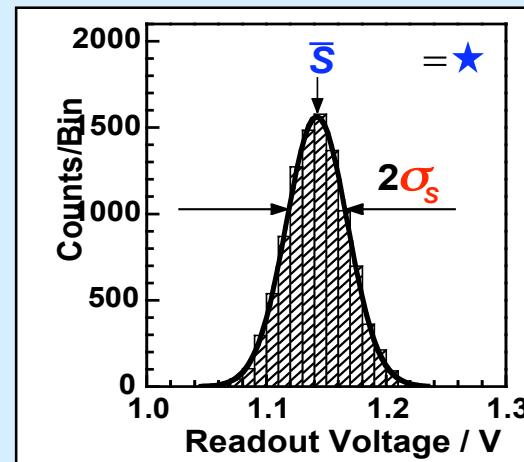
Not very  
much!!

Gated  
Integrator



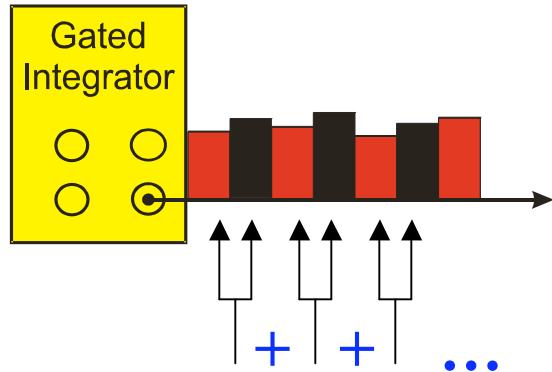
$S_1, S_3, \dots$

$$N = \left( \frac{N}{\sigma_N} \right)^2 = \left( \frac{N}{\sqrt{N}} \right)^2 \approx \left( \frac{\bar{S}}{\sigma_S} \right)^2 = N_{eff}$$

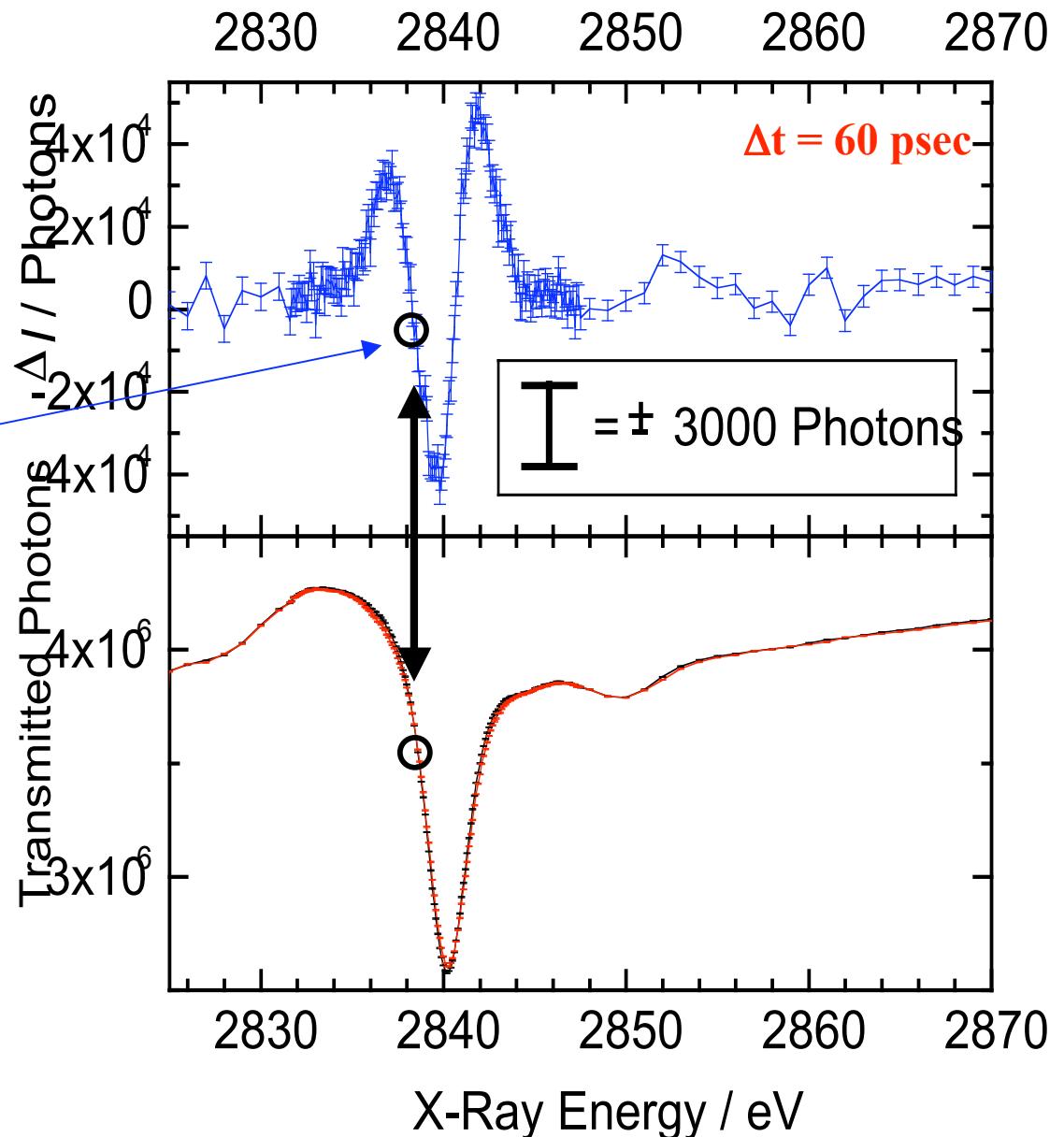


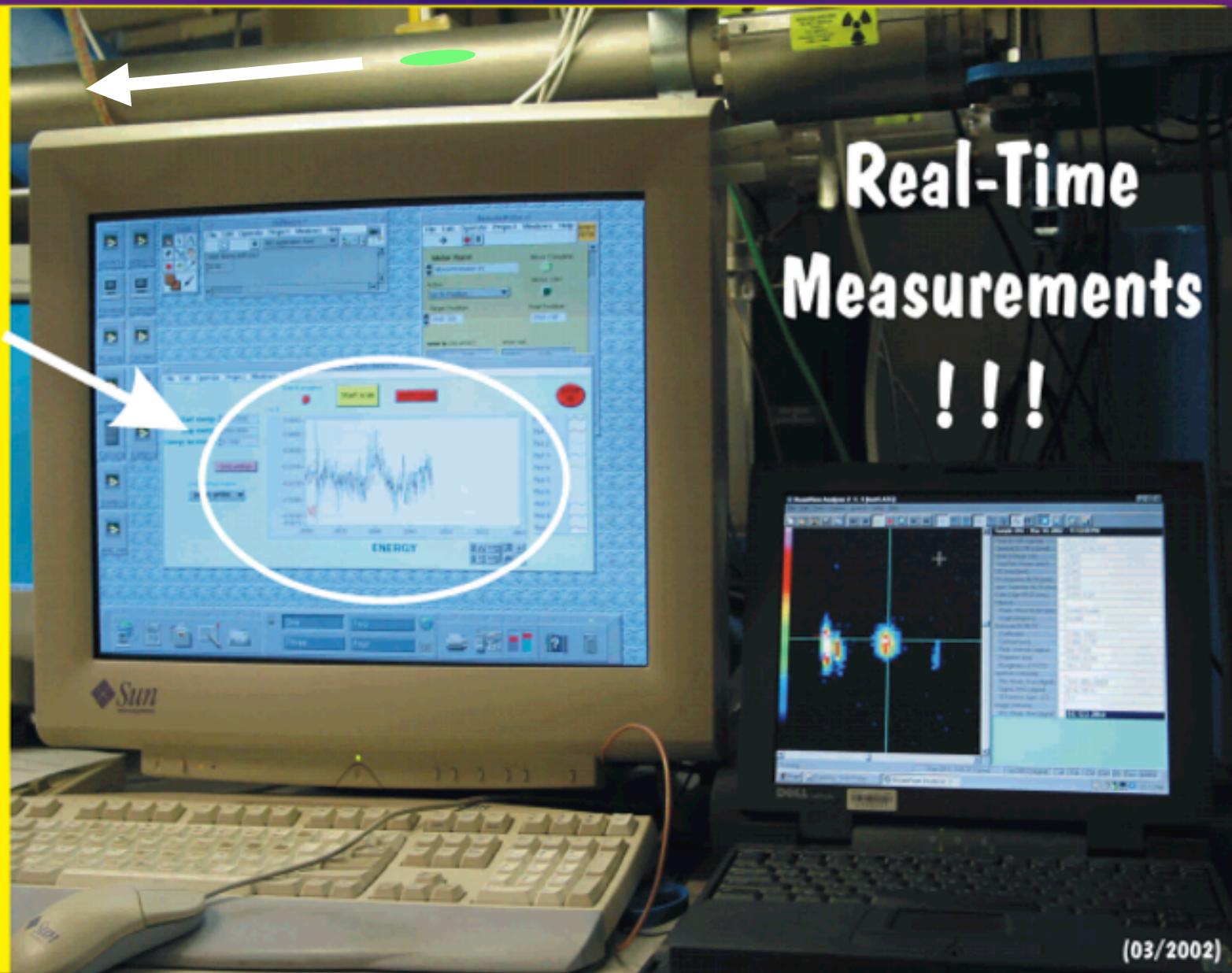
**SR is an extremely stable source**

## What can we measure with low intensity x-ray sources ?

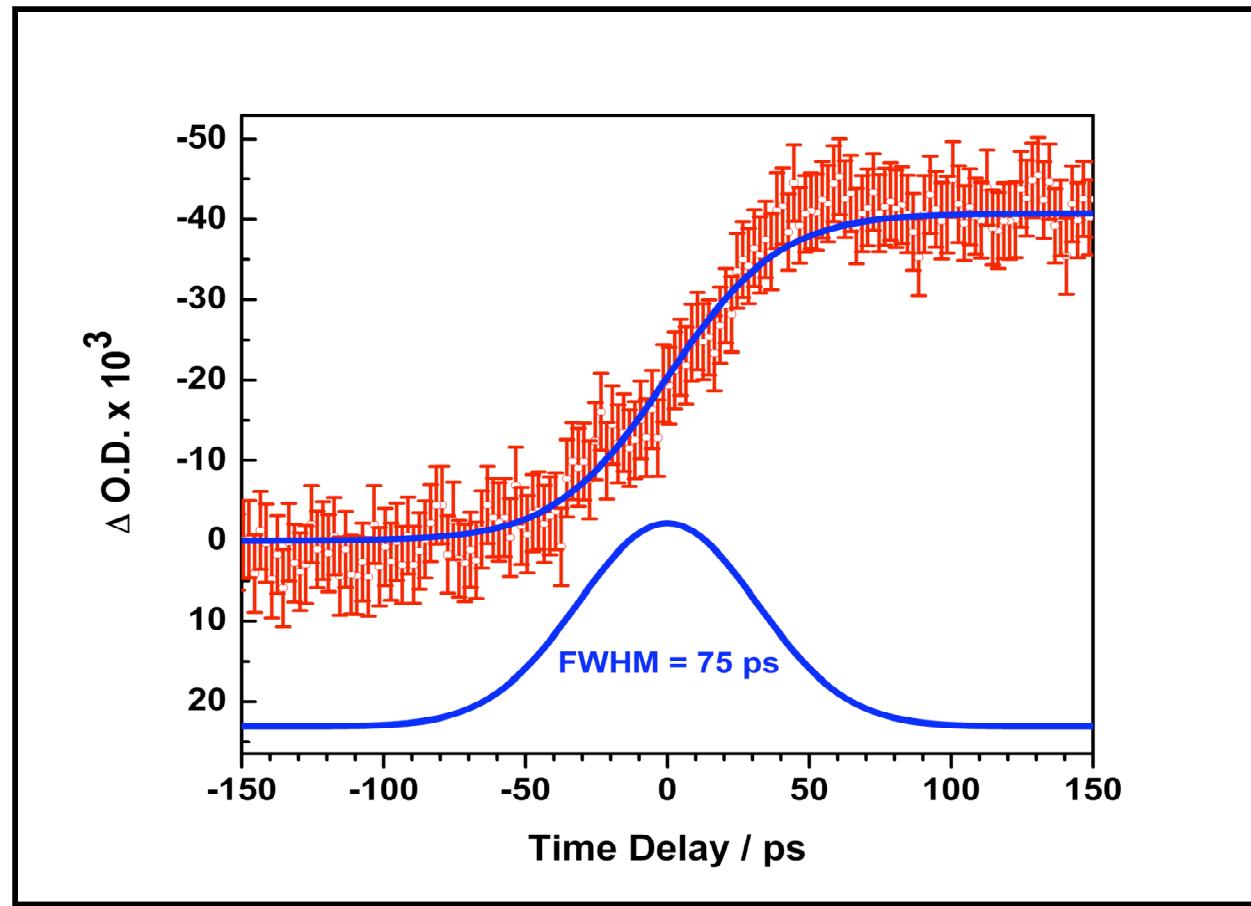


<1% photoinduced changes can be measured by XAS !





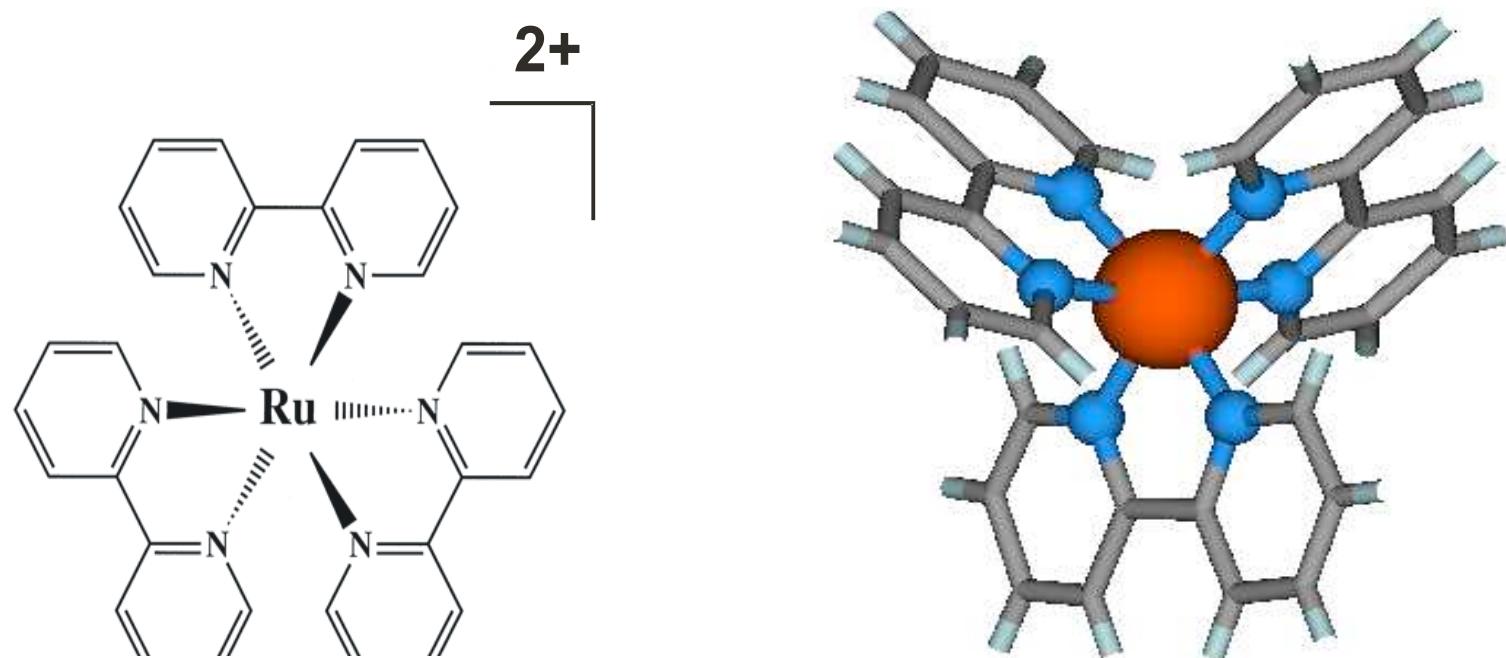
# Real-Time Laser/X-Ray Cross-Correlator



- Short scan times  $\leq 10$  min
  - Adjustable time delay between laser and x-ray pulses up to nsec and more
- Timing jitter  $\leq 10$  ps accuracy**

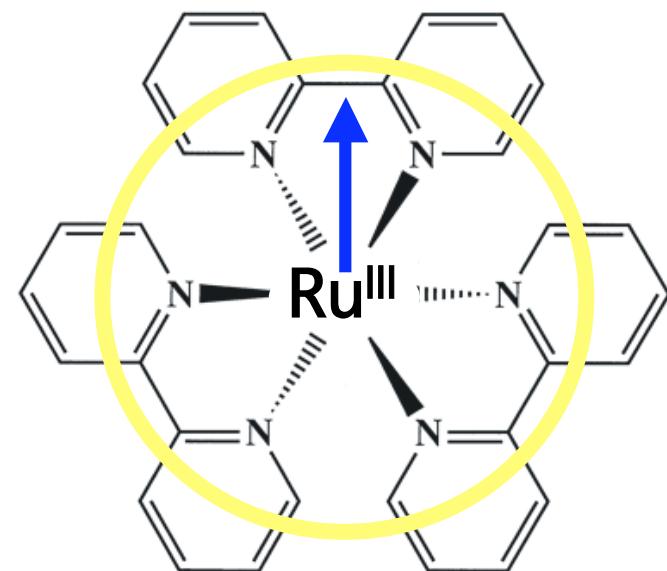
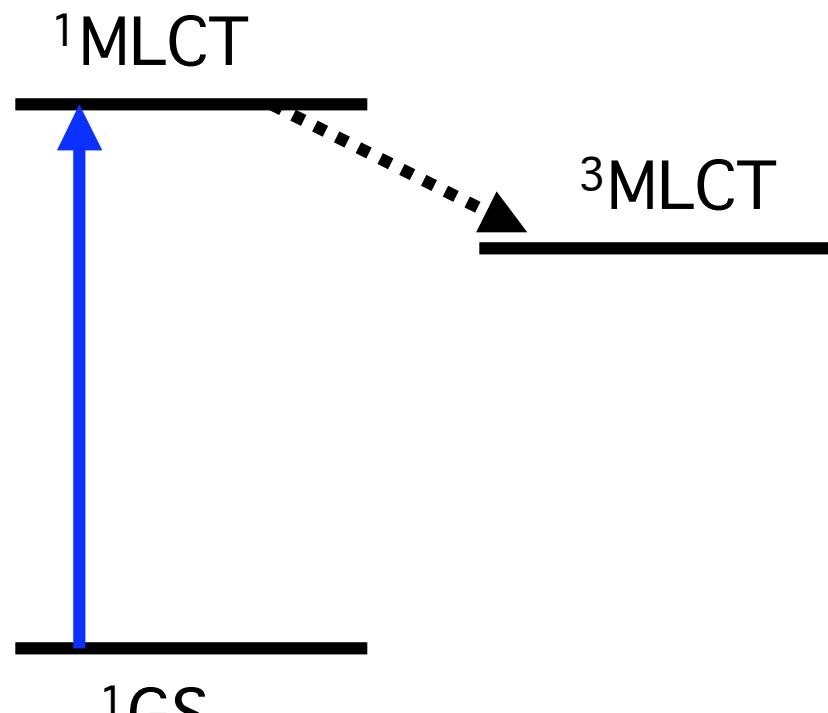
# *Photochemistry of Aqueous $[Ru(bpy)_3]^{2+}$*

- H-atom of coordination chemistry
- Photosensitizer
- Solar Cells
- Catalyst in Redox-Reactions
- Marker in Biology,...



# *Photochemical Cycle of $[Ru^{II}(bpy)_3]^{2+}$*

ISC Time  
ca. 40 fs (Bhasikuttan *et al.*, 2002)



$D_3$

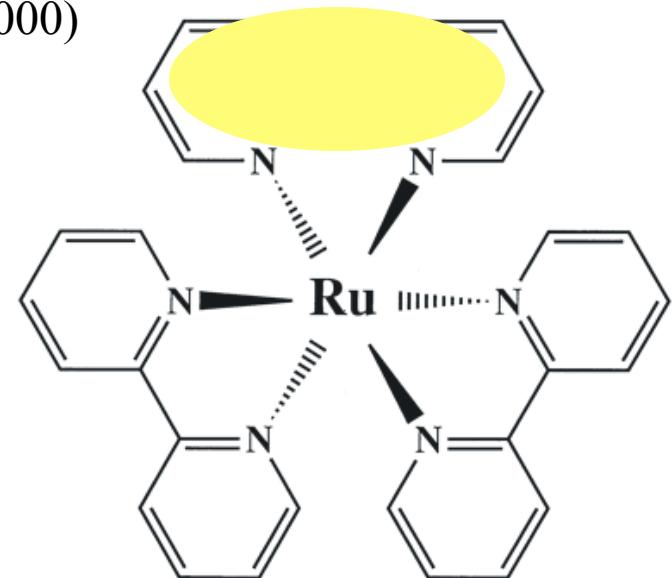
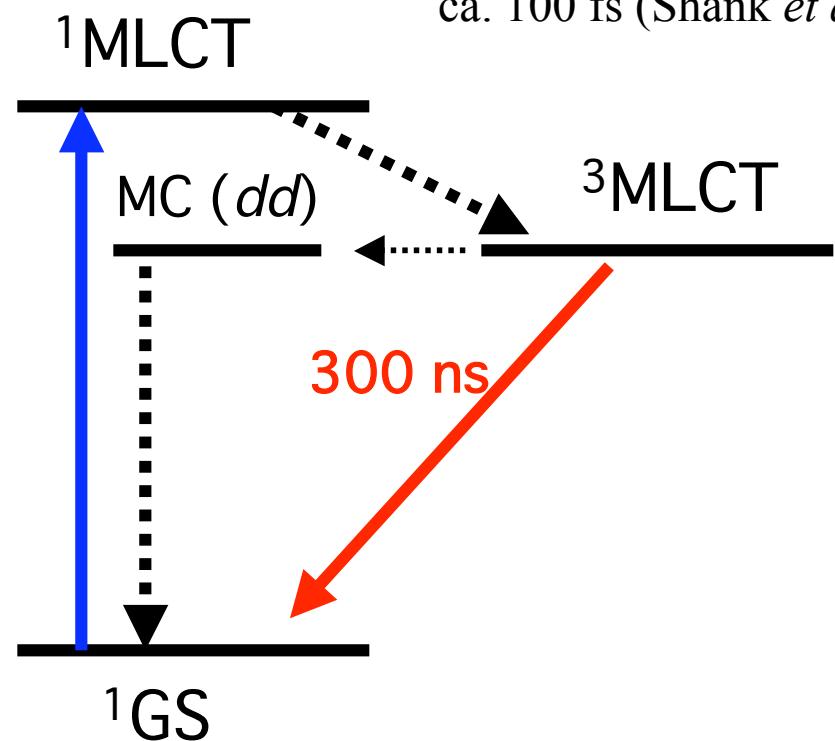
# *Photochemical Cycle of $[Ru^{II}(bpy)_3]^{2+}$*

ISC Time

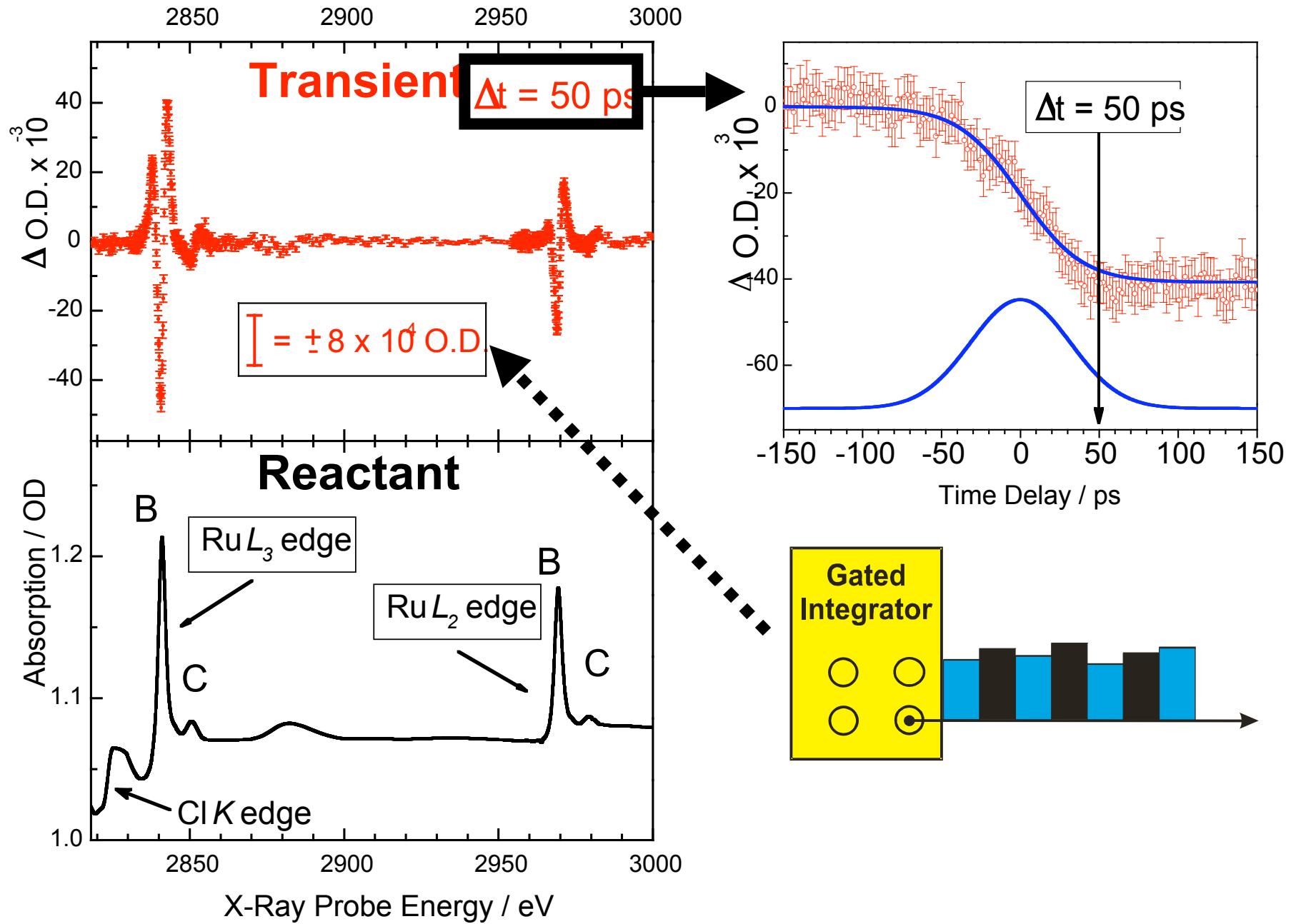
ca. 40 fs (Bhasikuttan *et al.*, 2002)

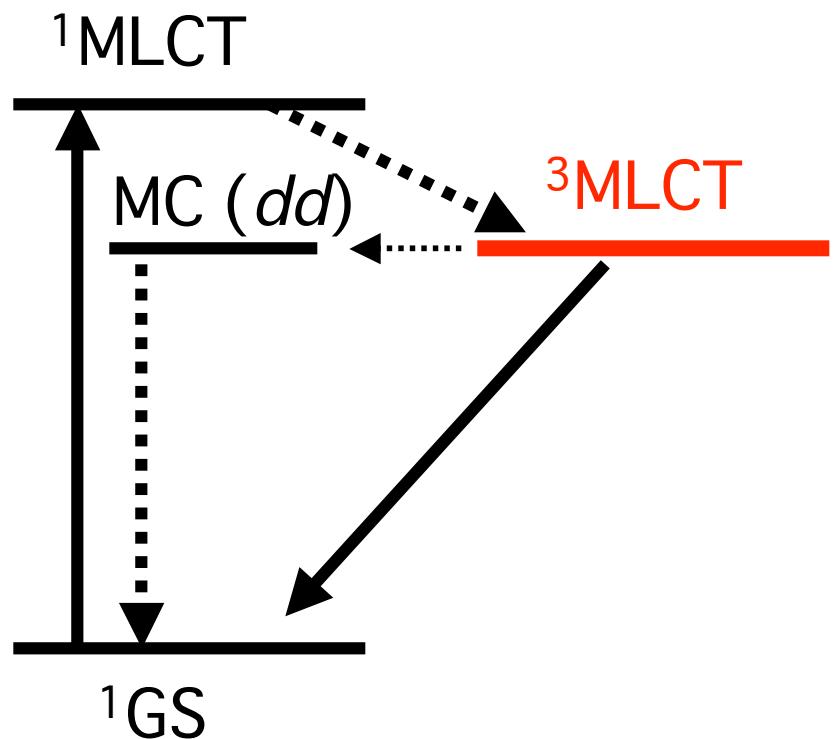
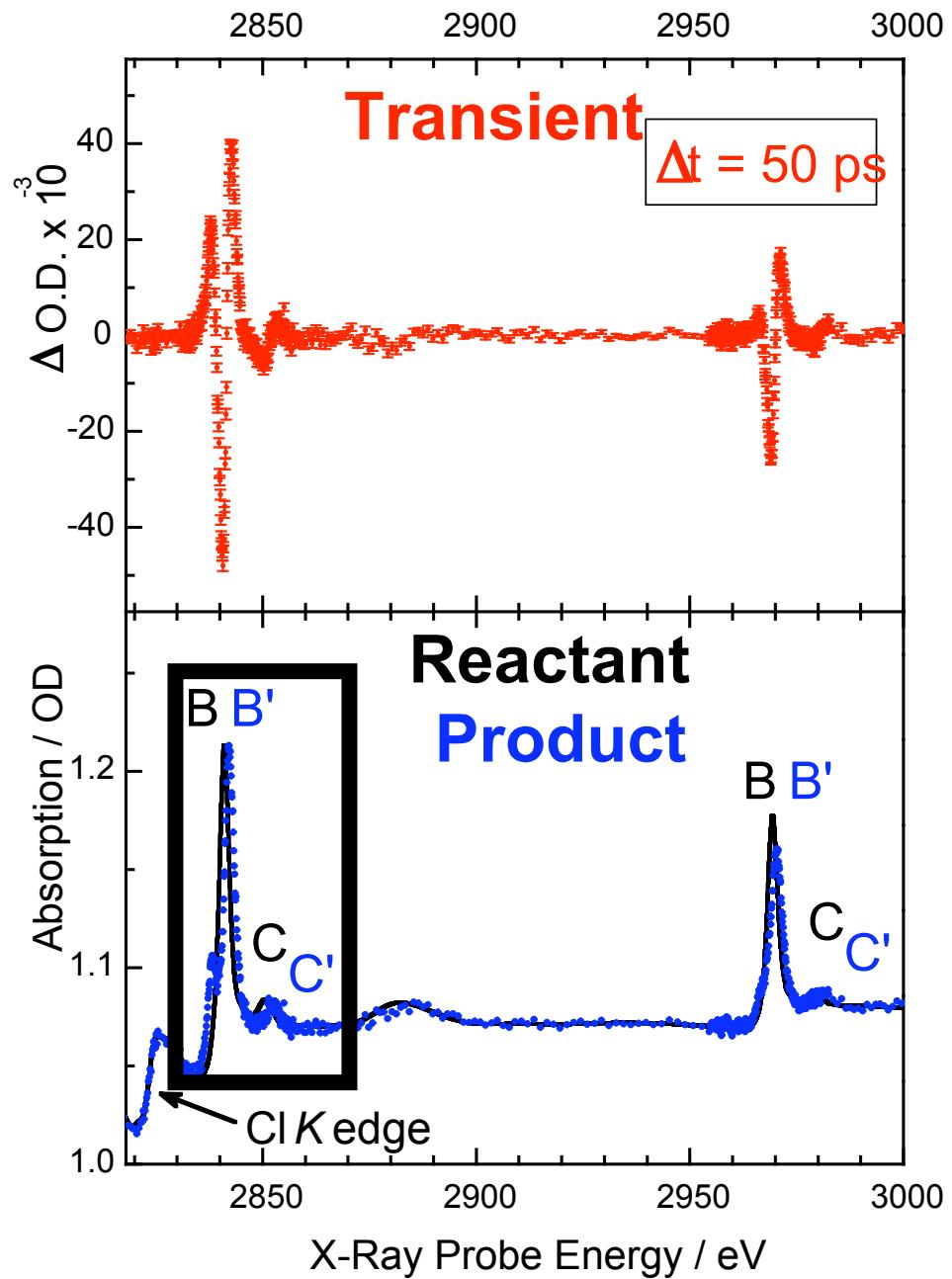
e<sup>-</sup> Localization Time(s):

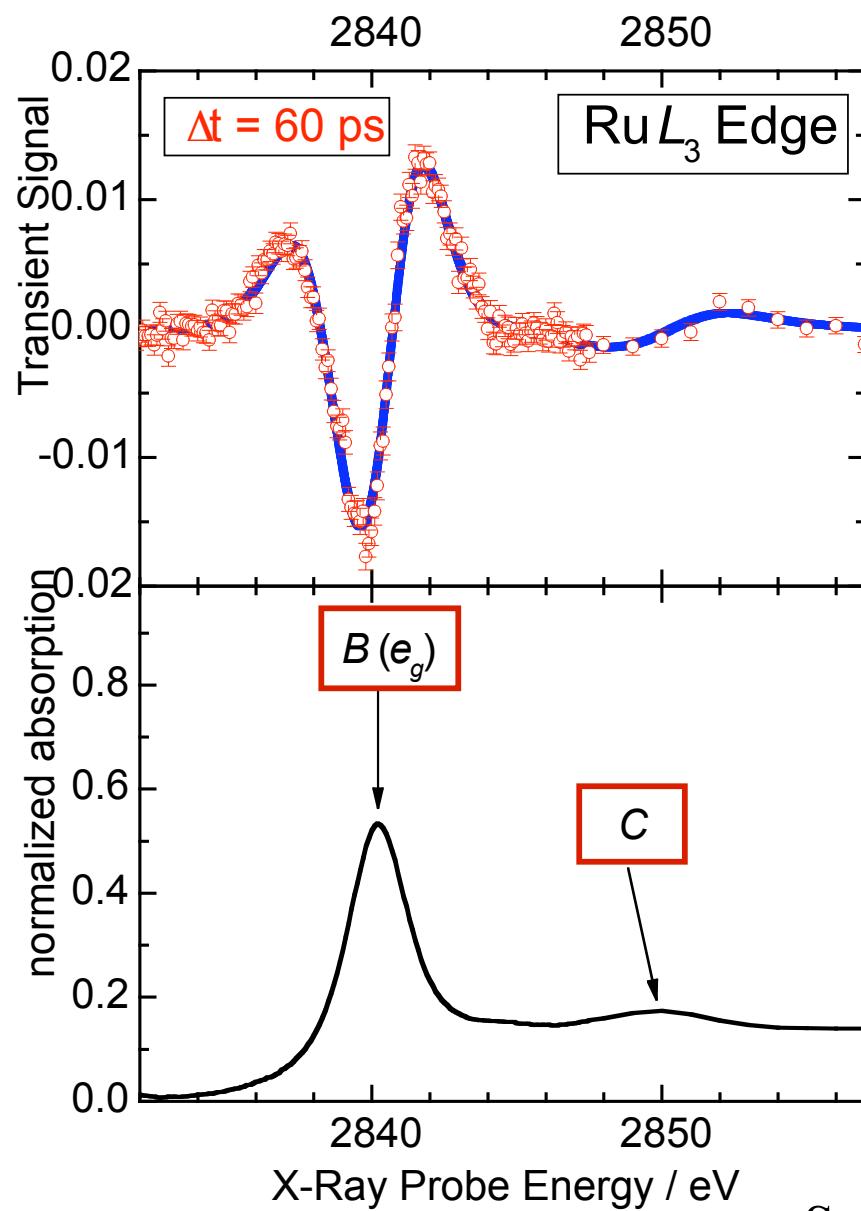
ca. 100 fs (Shank *et al.*, 2000)



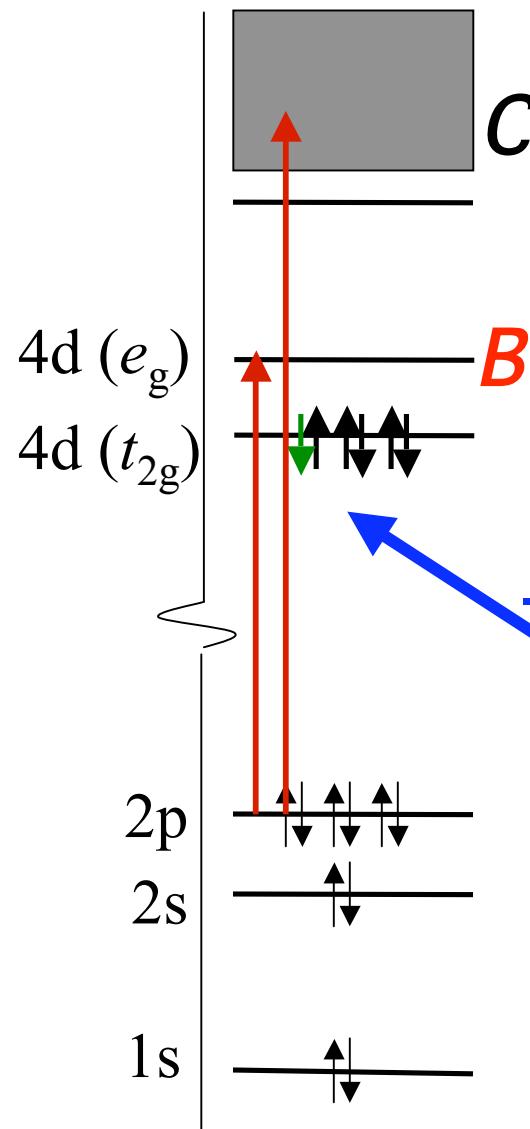
$C_2$



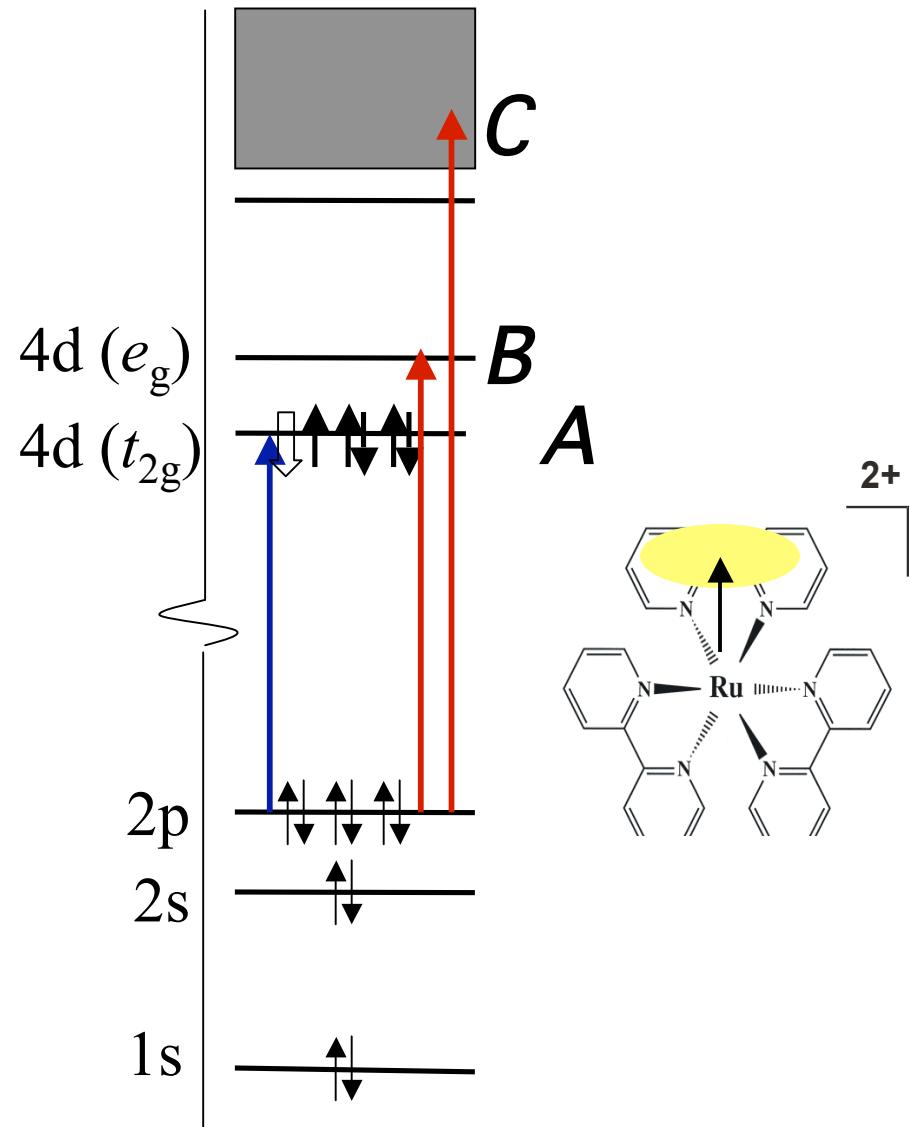
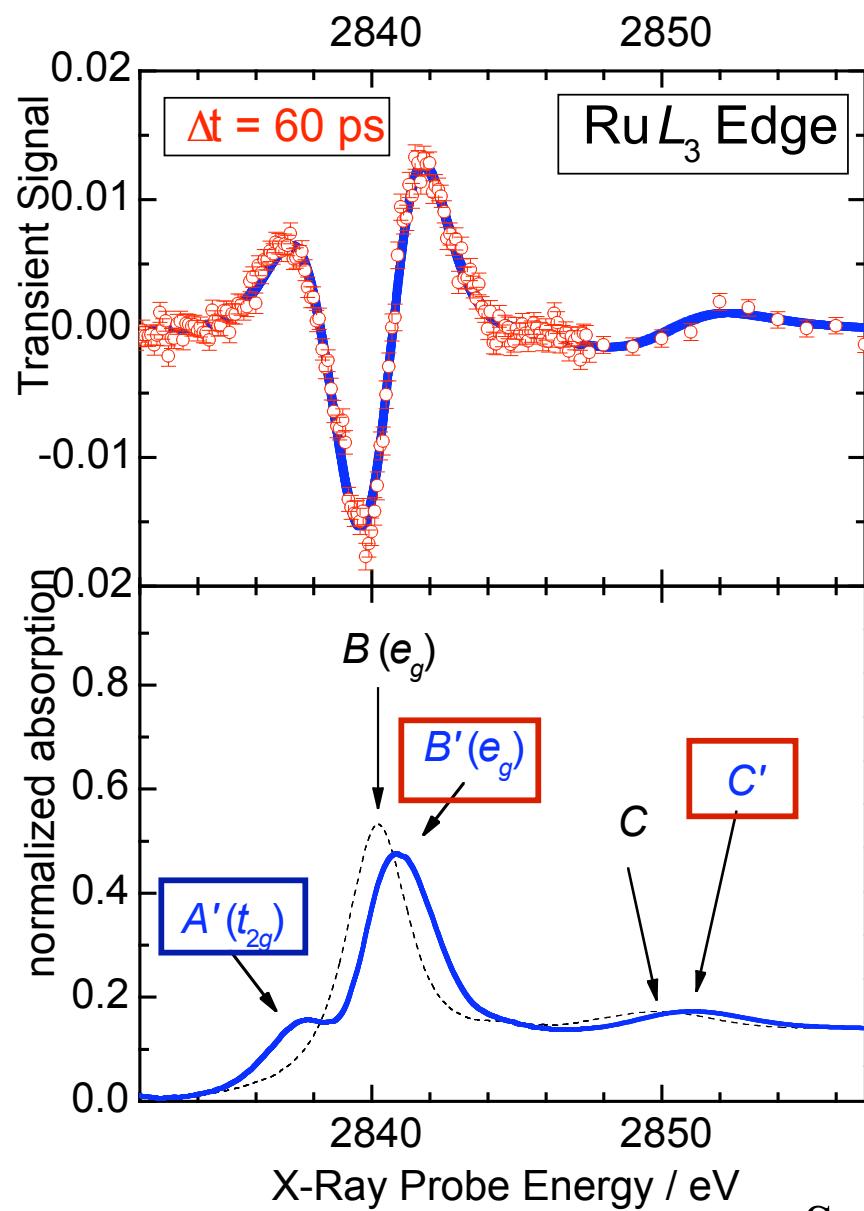


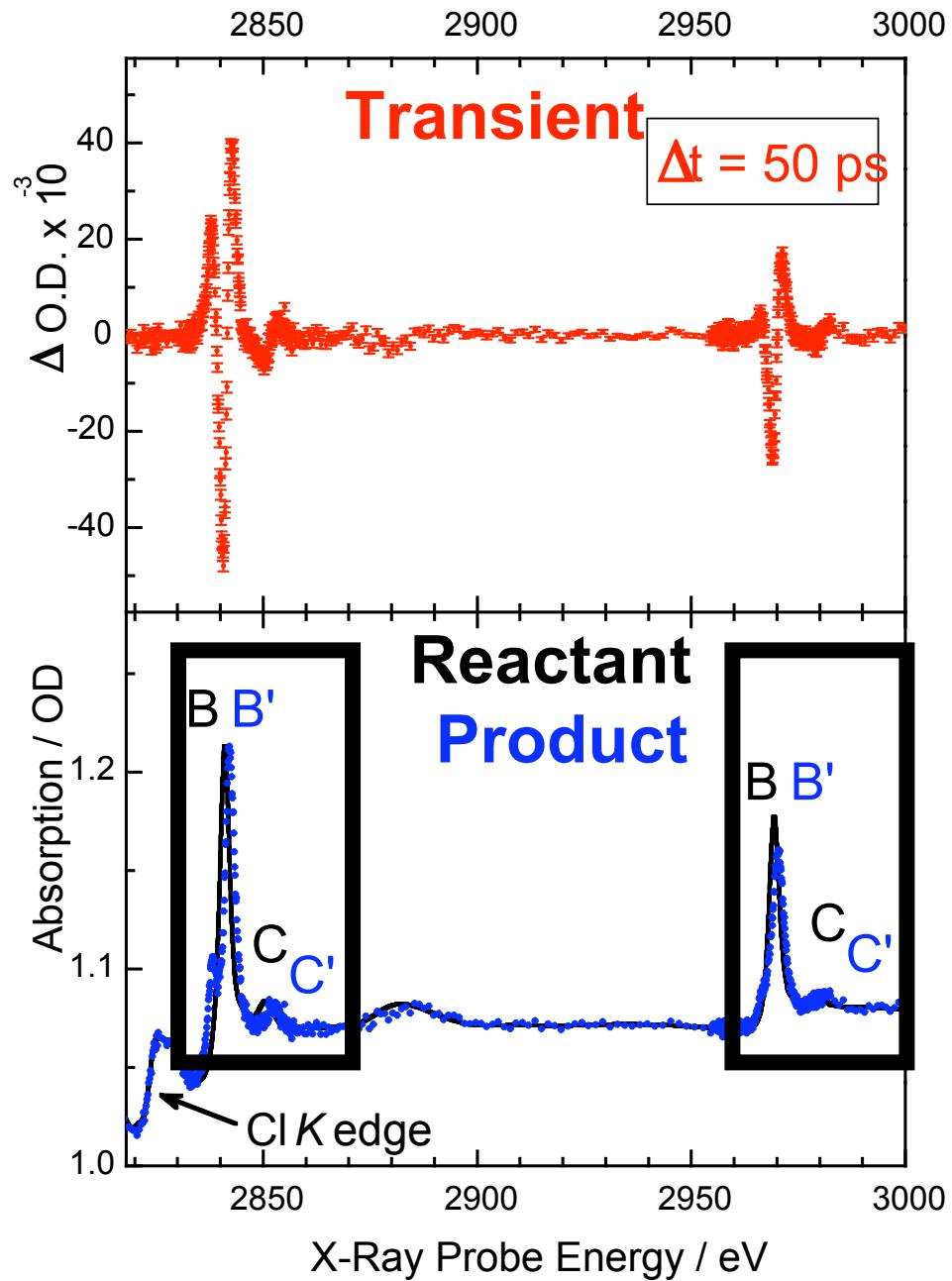


Ru<sup>II</sup>



Ru<sup>III</sup>





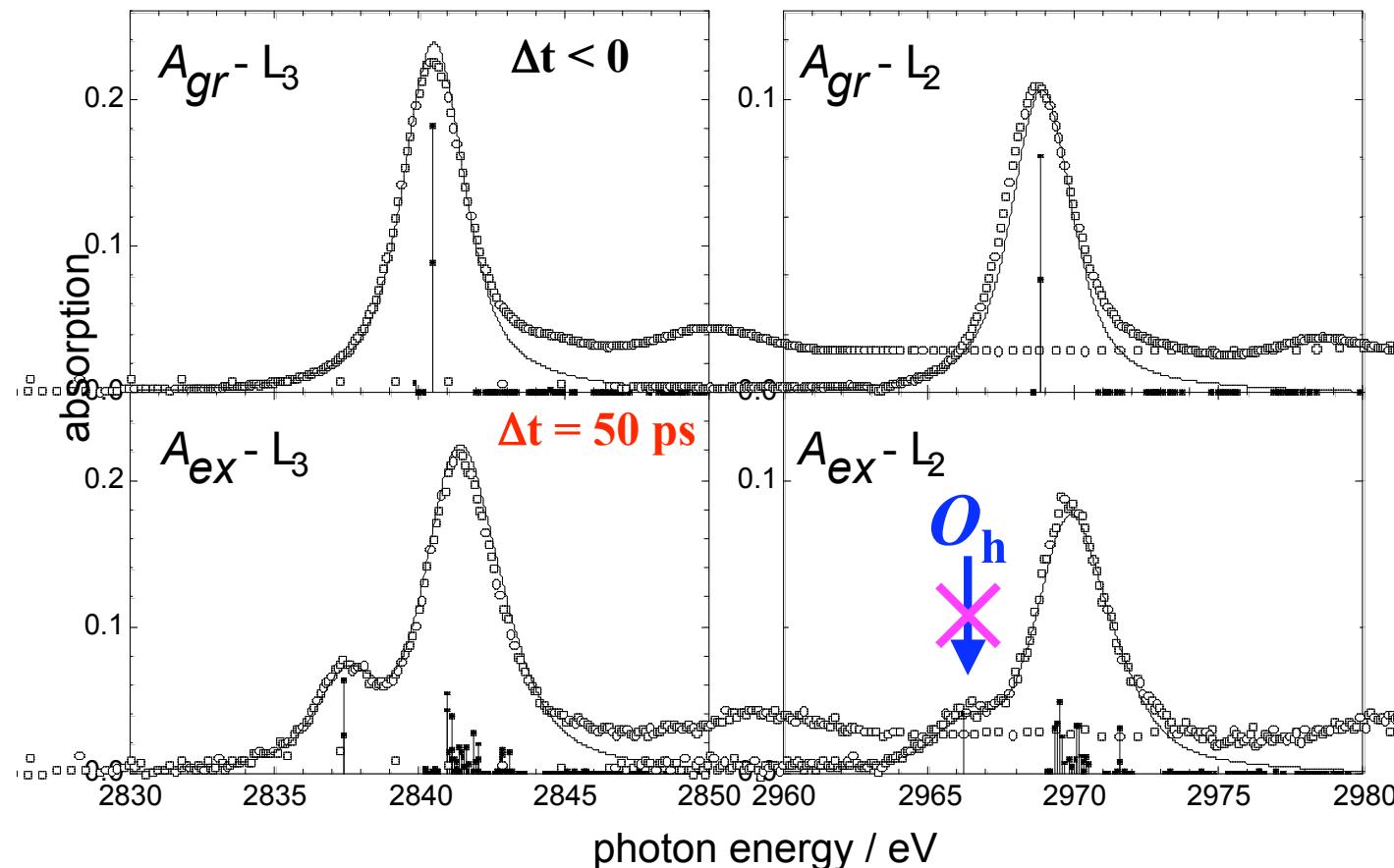
Structural Information via XANES

Ground and Excited States

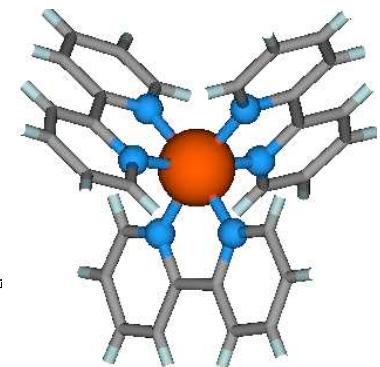
$$H = H_{atom} + H_{Cryst.}$$

$H_{atom}$  includes e-e correlations, spin-orbit coupling

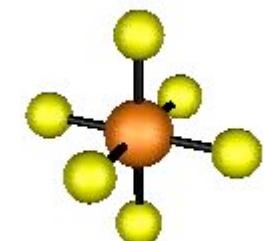
$H_{Cryst.}$  includes octahedral and trigonal field contributions



$D_3 :$   
 $\text{Ru}(\text{bpy})_3$



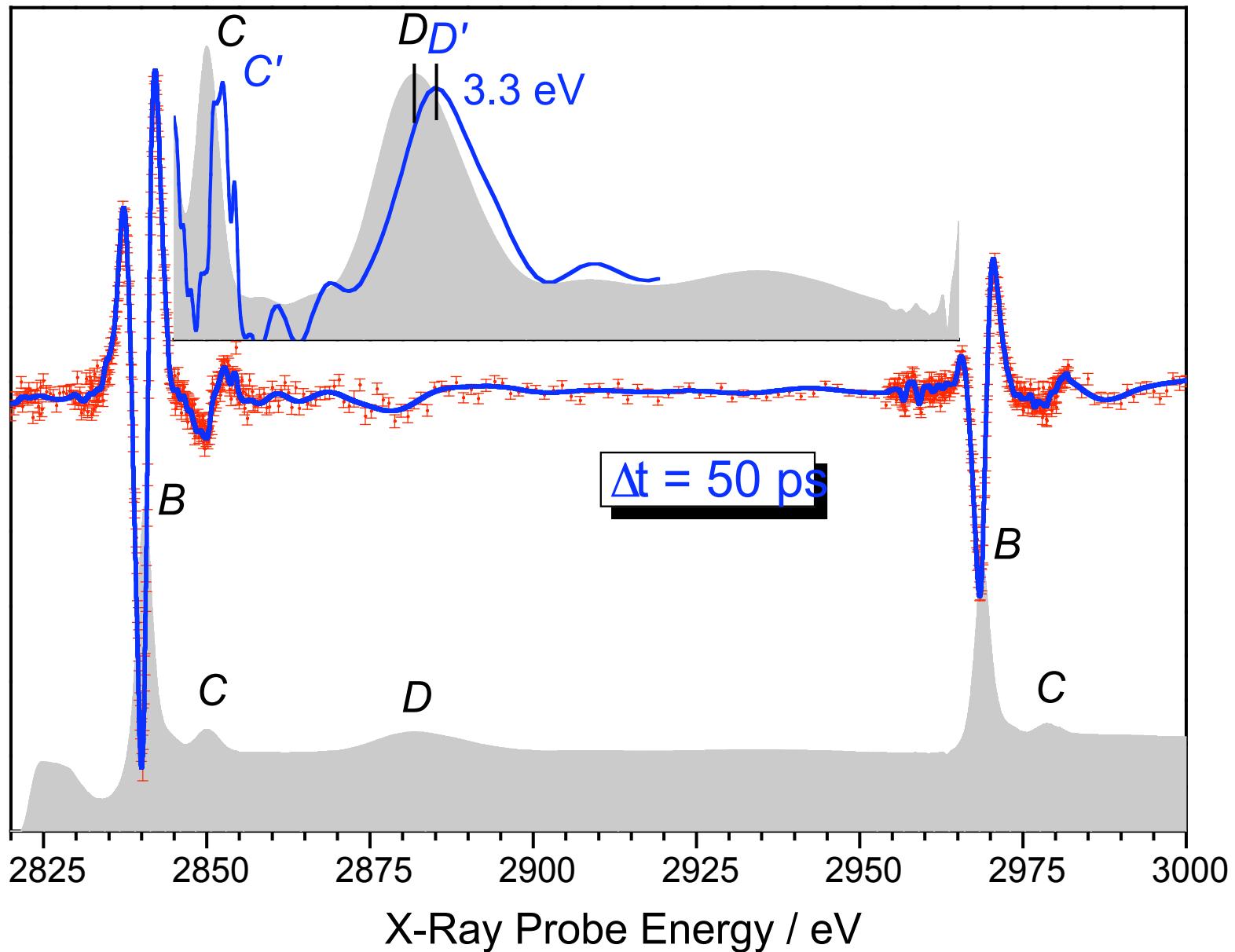
$O_h :$   
 $\text{Ru}(\text{NH}_3)_6$



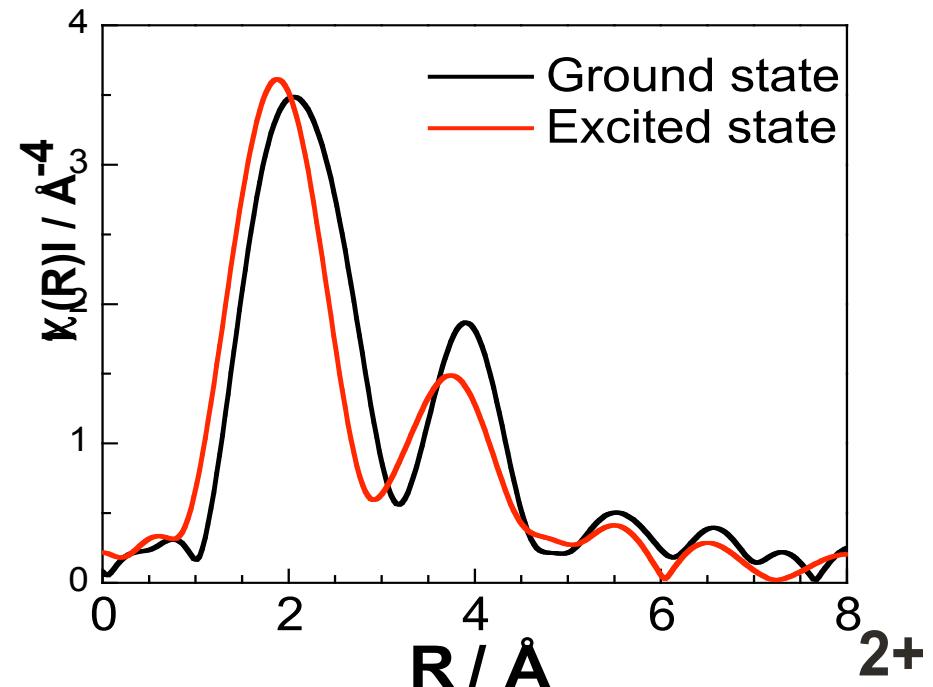
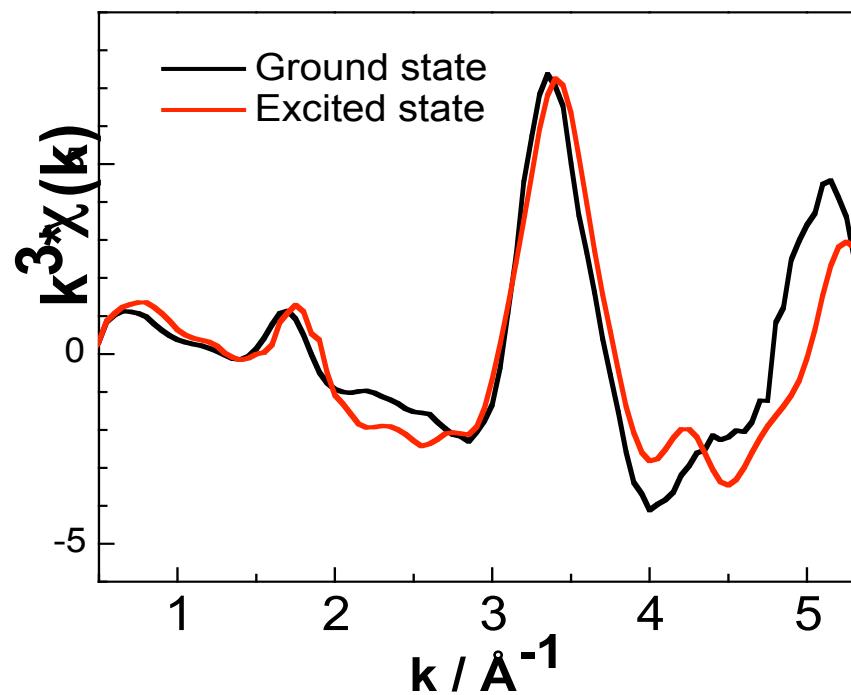
?? Why not  $C_2$  (localized electron) ??

M. Saes, Ph.D. thesis (2004)

# *Transient Structure from EXAFS*

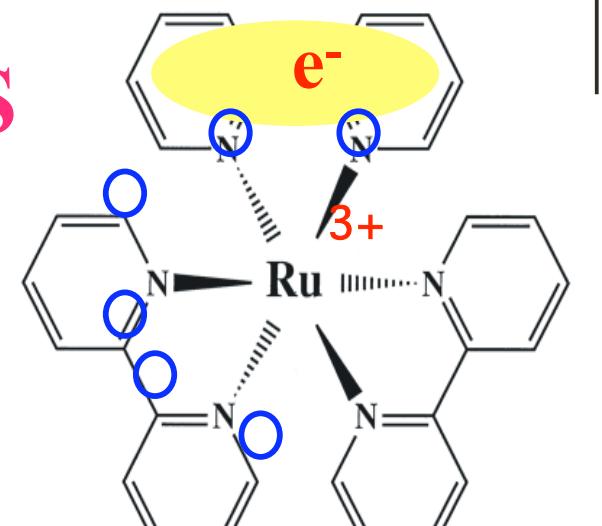


# Analysis of Local Structural Changes ( $\Delta t = 50$ ps)



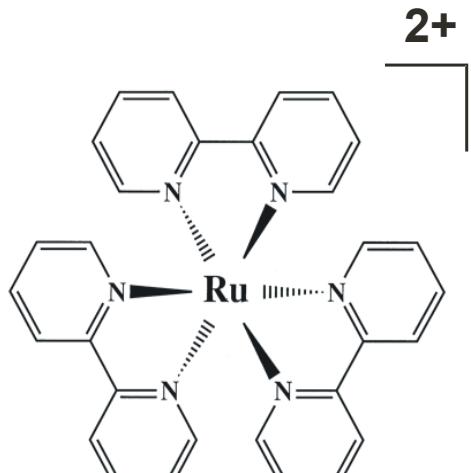
## Structure from transient XAFS

- Reduced Ru-bpy distances
- $D_3 \leftrightarrow C_2$  ?!



# Run XANES calculations on Ru(bpy)<sub>3</sub>

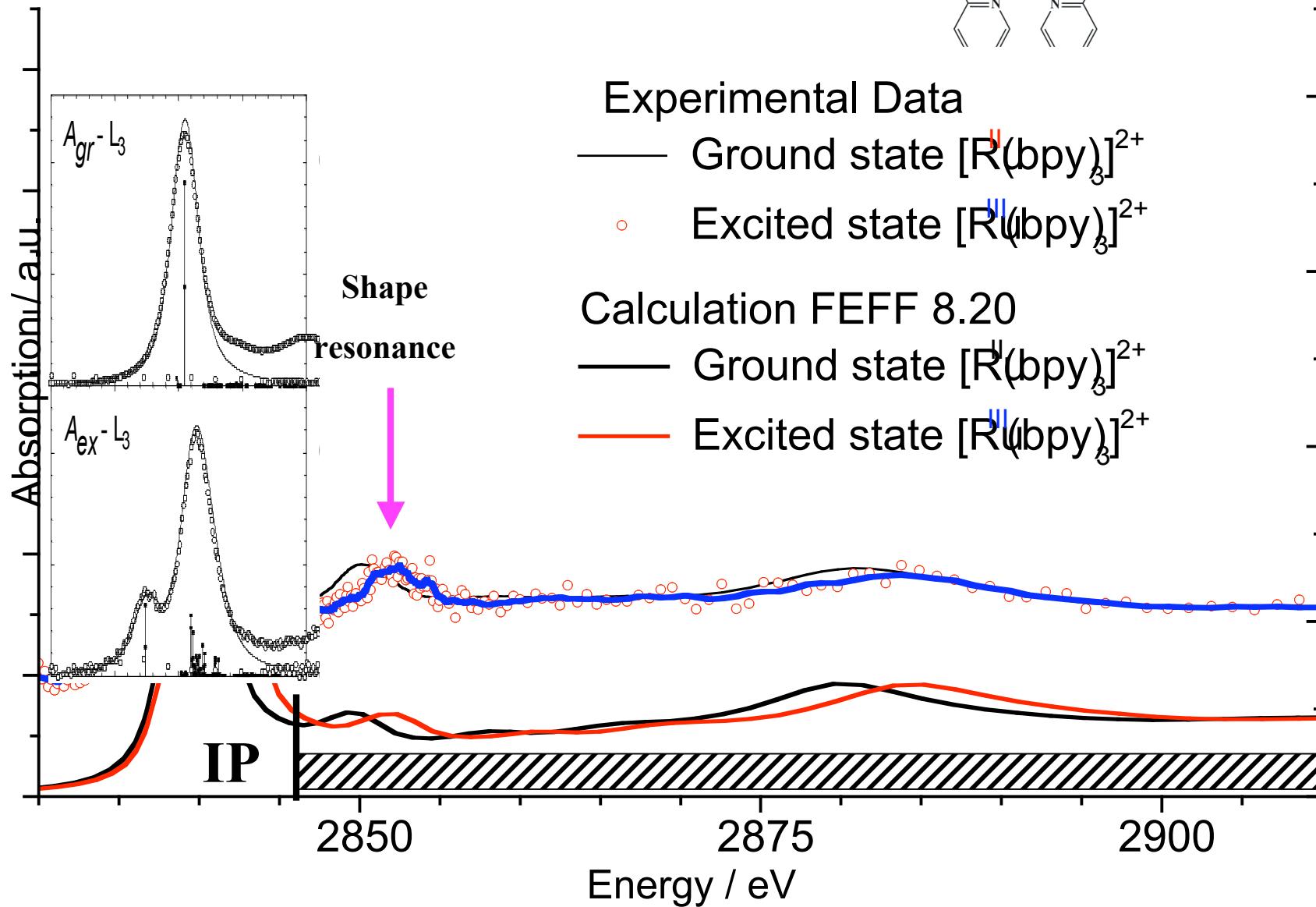
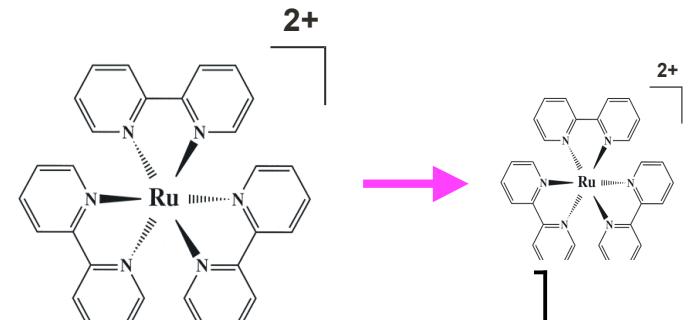
- Change Ru charge ( $2+ \rightarrow 3+$ )
- calculate different scenarios:



- 1.) move one bpy closer ( $C_2$ )
- 2.) move one closer and two away ( $C_2$ )
- 3.) ... ...does not work
- 4.) shrink the molecule ( $D_3$ )

# Shrink the molecule (balloon)

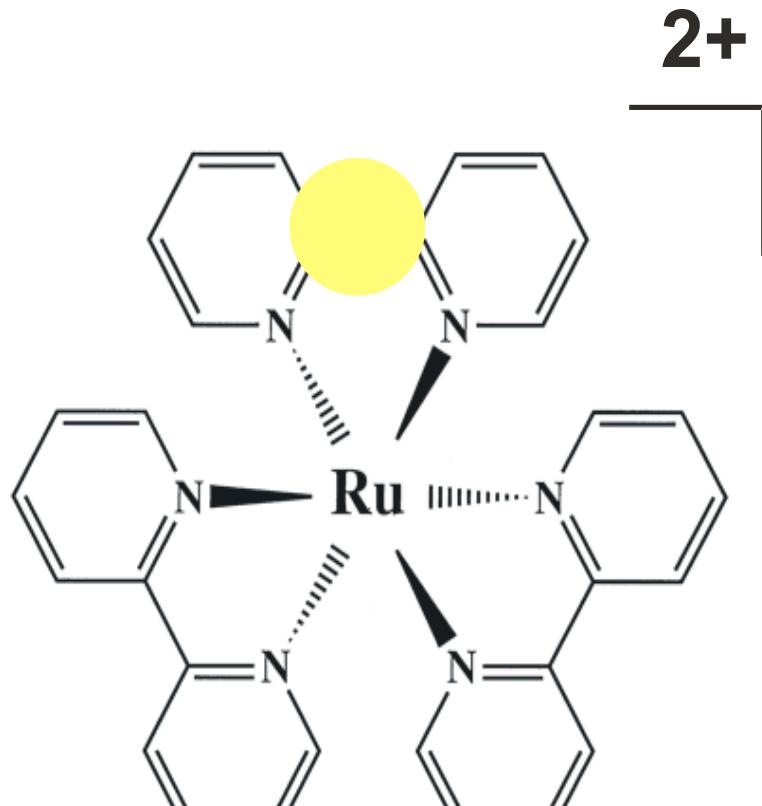
$$\Delta R (\text{Ru-N}) = -0.06 \text{ \AA}$$



# Interligand Electron Transfer

e.g.: Sundstrom (JPC B 108, 2862, 2004):

ILET times: 1 – 100 ps



$kT > 400 \text{ cm}^{-1}$

Ru-N stretch:  $318 \text{ cm}^{-1}$

$\lambda_{\text{exc}} = 400 \text{ nm}$

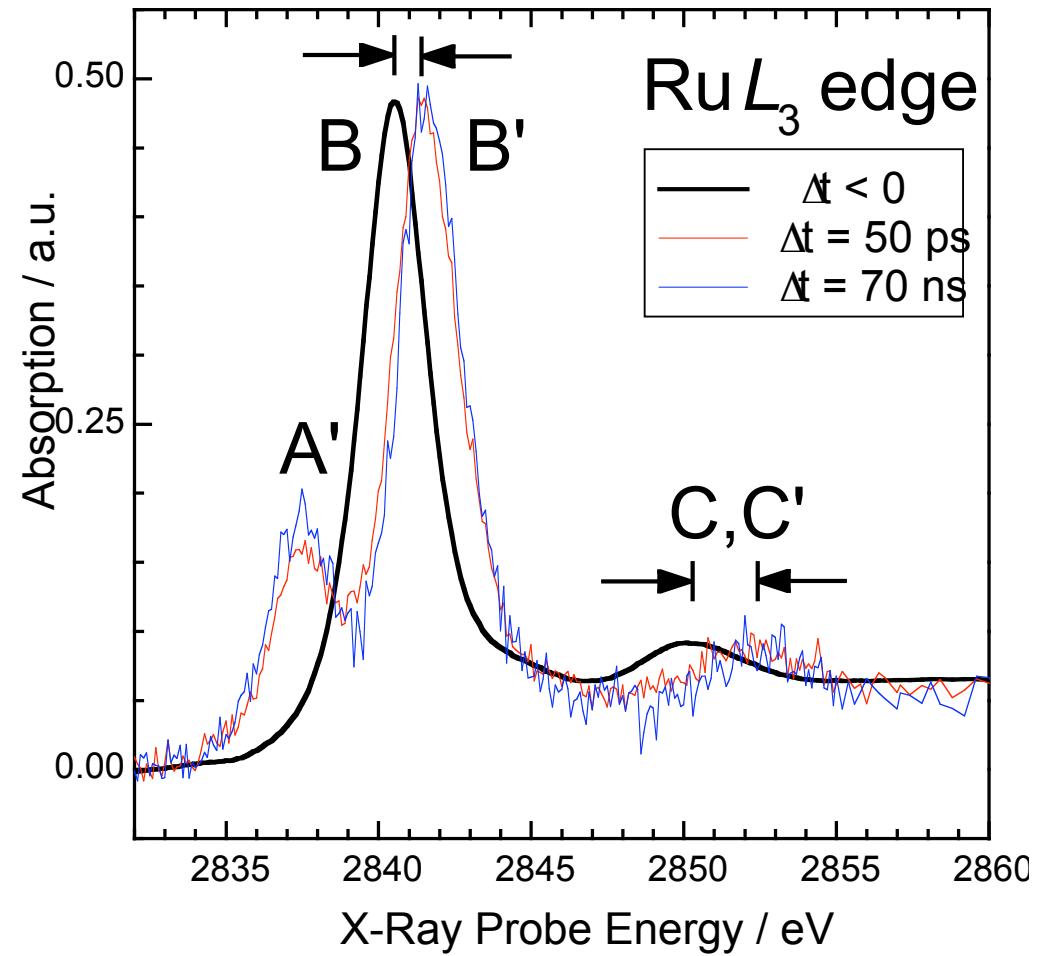
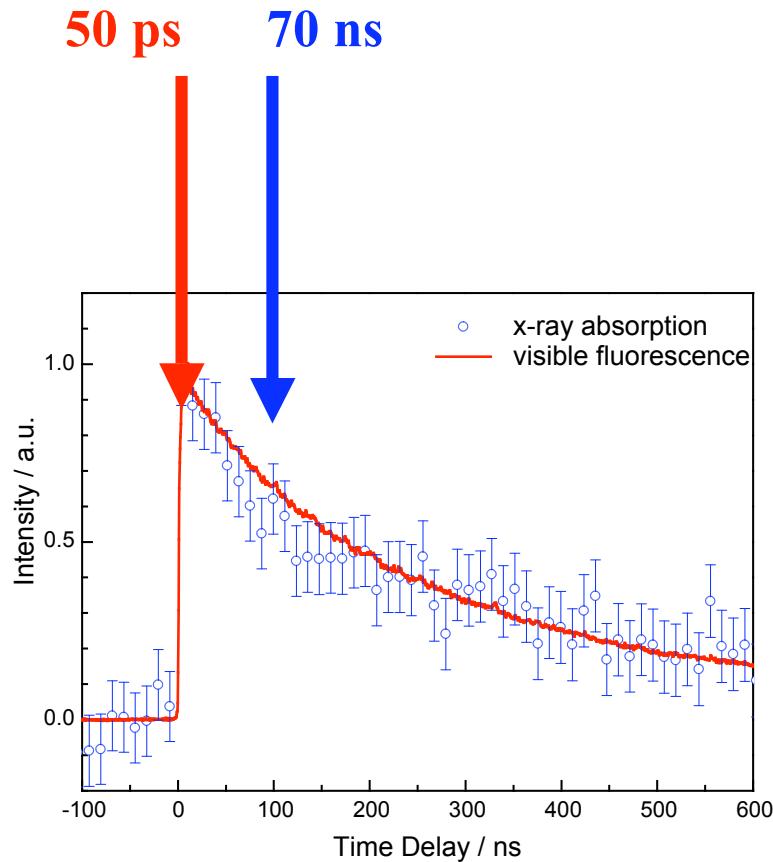
$E_{\text{excess}} > 4000 \text{ cm}^{-1}$

May preserve  $D_3$  symmetry,  
if fast enough ...

... on the other hand:  
can not (yet) fully exclude  $C_2$   
(analysis in progress...)

# Kinetic Study of Photoexcited Ru(bpy)<sub>3</sub>

- agreement with optical studies
- no significant change on the ps – ns time scales

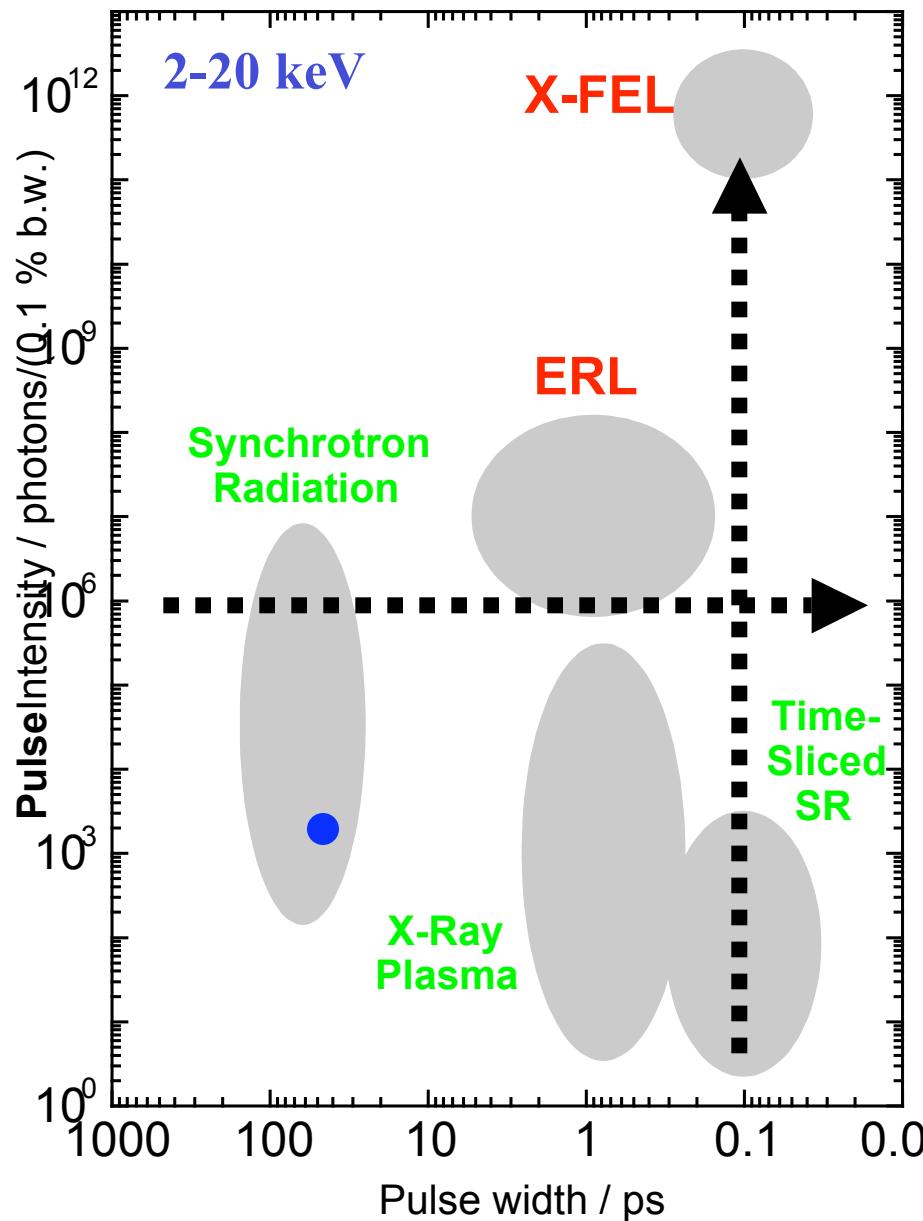


## Summary

- Picosecond XAFS in the Condensed Phase
  - **hypothesis: ILET may retain  $D_3$ -symmetry**
- Optical-X-ray cross-correlator down to fsec
- fsec resolution not a problem  
(only  $10^6$  x-ray photons/data point !)
- Dilute systems (1 mmol → chemistry and biology)
- non\_reversible reactions

*Universal method for detecting ultrafast  
**(non) reversible structural and electronic changes***

## Pulsed X-Ray Sources

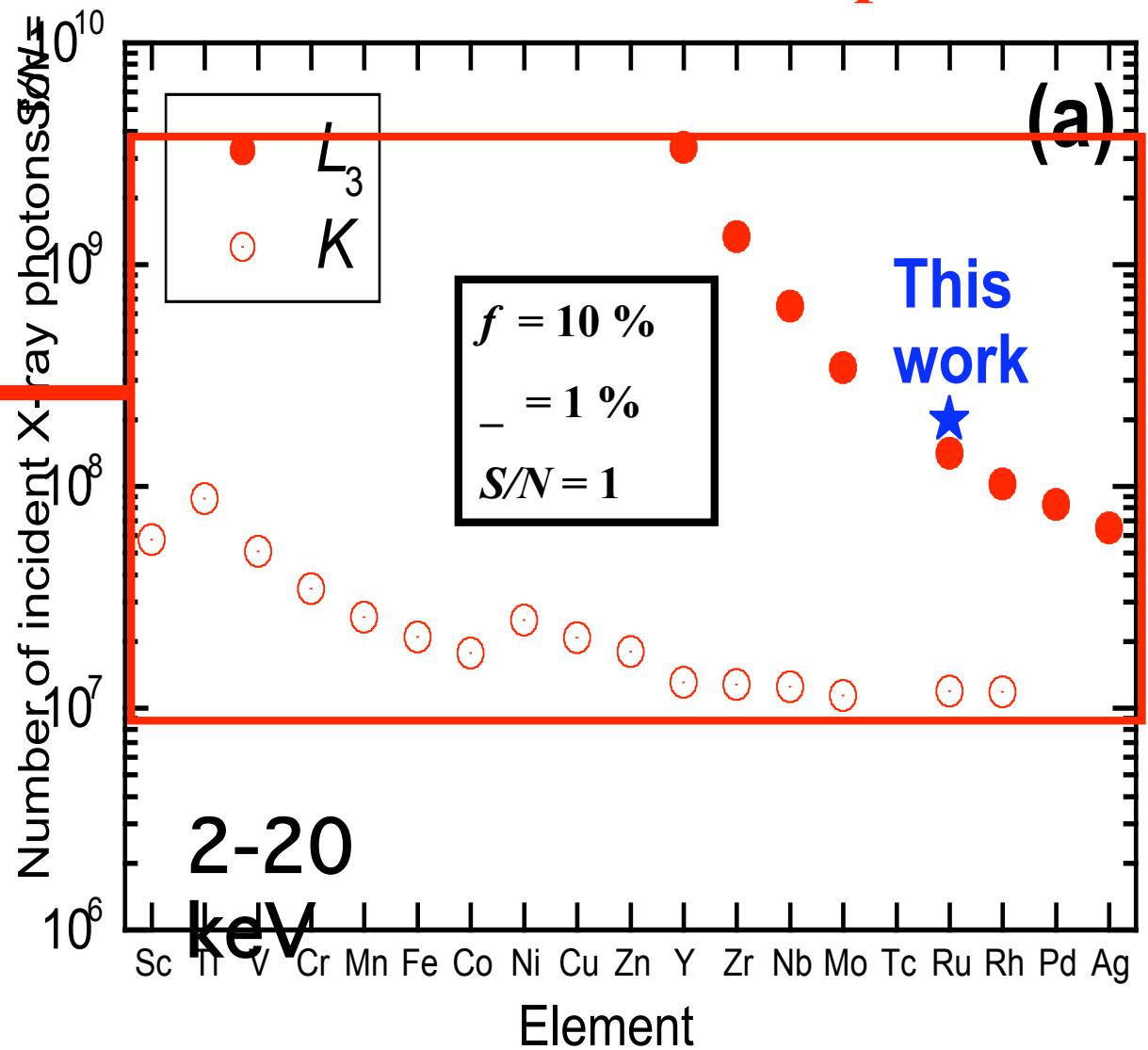
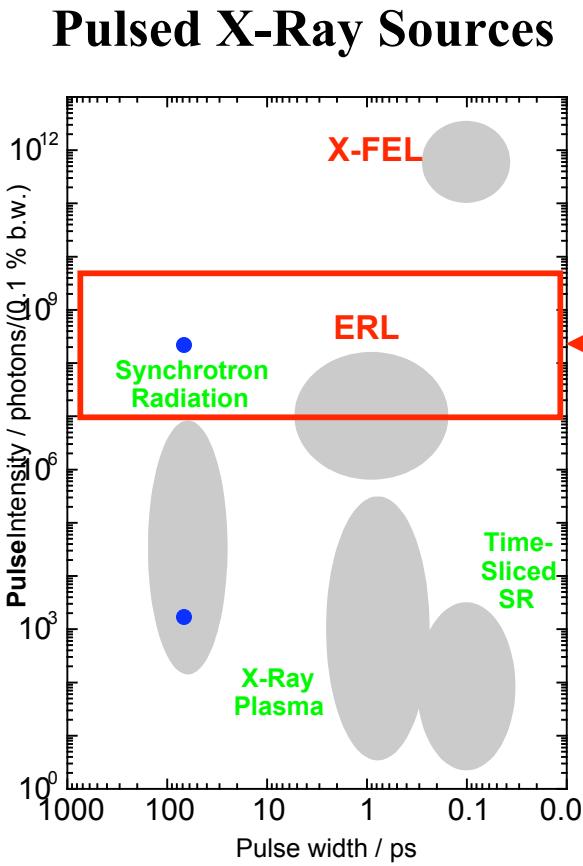


**What can we  
measure with  
existing/future pulsed  
x-ray sources ??**

**We now have  
experimental results  
to extrapolate !!**

**Examples:**  
*EXAFS on Transition  
Metal Compounds*

# Ultrafast EXAFS on Transition Metal Compounds



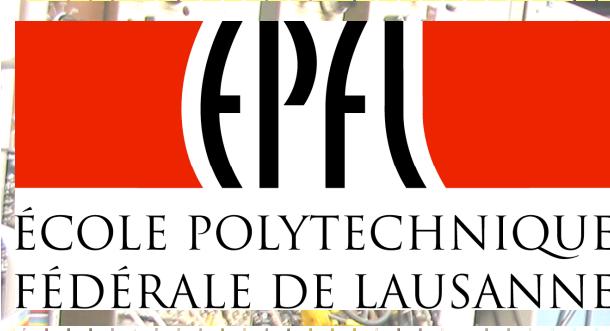
Bressler and Chergui, Chem. Rev. **104**, 1781 (2004)

# Personal Outlook

## *Structural Dynamics with femtosecond x-rays*

- **Science** (Condensed Phase Dynamics)
  - Coordination Chemistry
  - Biologically Relevant Systems
  - *Solvation Dynamics*
- → **Ultrafast Processes in Many-Body Systems**
- **Instrumentation** (shorter and more intense x-rays)
  - sub-ps streak camera (2004-6)
  - time-sliced 100 fs SR (ALS, SLS, 2006-)
  - **X-FEL**
- → ERL facilities (**LUX**,...)

# Members and Collaborators:



ÉCOLE POLYTECHNIQUE  
FÉDÉRALE DE LAUSANNE

## EPF-Lausanne:

Melanie Saes → SLS  
→ Bartosz Sobanek  
Wojciech Gawelda  
Maik Kaiser  
Alexander Tarnovsky  
Majed Chergui

## Utrecht University

F. M. F. deGroot



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Rafael Abela  
Daniel Grolimund  
Steven Johnson



## Advanced Light Source

Philip Heimann  
Robert Schoenlein

## UC Berkeley

Roger Falcone  
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Donnacha Lowney



CHF: Swiss NSF,

